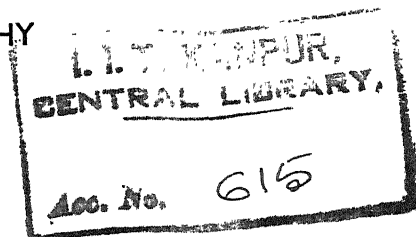


CONFIGURATIONAL STATISTICS OF MACROMOLECULAR SYSTEMS

A Thesis Submitted
In Partial Fulfilment of the Requirements
for the Degree of
DOCTOR OF PHILOSOPHY

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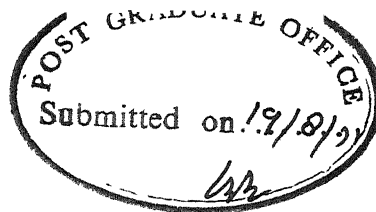
BY
UMA KAPUR

to the

DEPARTMENT OF PHYSICS
INDIAN INSTITUTE OF TECHNOLOGY KANPUR
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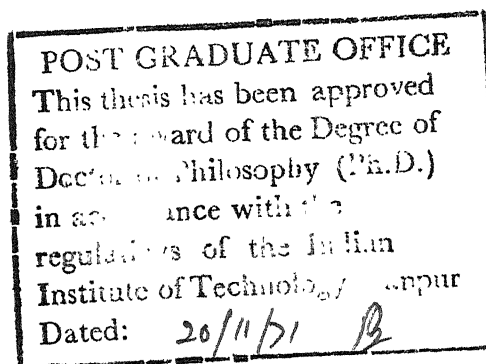


CERTIFICATE

Certified that this work on "Configurational Statistics of Macromolecular Systems" by Uma Kapur has been carried out under my supervision and that this has not been submitted elsewhere for a degree.

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SYNOPSIS

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CONFIGURATIONAL STATISTICS OF MACROMOLECULAR SYSTEMS

Polymer chains consist of a large number of like units and because of the presence of internal rotations around single bonds, are capable of taking almost an infinite number of conformations in space. This necessitates a statistical approach in studying their physical behaviour. The dimensions of polymer chains are most conveniently characterized in terms of the mean square end-to-end distance $\langle R_n^2 \rangle$, where n is the number of links. The knowledge of this distance is important in developing the equation of state for rubber elasticity, for deriving equations expressing intrinsic viscosity in terms of chain length, for interpreting light scattering data from dilute solutions and for promoting the growth of other important theoretical concepts. In the first chapter, we have discussed these aspects and briefly summarised the theoretical approach followed by other workers in calculating $\langle R_n^2 \rangle$.

In the second chapter, a random-walk model for hydrocarbon type chains with short range correlations is given. The three possible orientations of a hydrocarbon type chain have different probabilities depending on whether they are placed in a trans or in two possible gauche positions. The energy difference between a gauche and a trans sequence of three links is taken as ϵ . $\langle R_n^2 \rangle$ is calculated by describing a random walk on a diamond lattice. The progress of the chain is governed by two probability parameters. The mathematical methods of Markoff chain are used to calculate $\langle R_n^2 \rangle$ for an oriented chain. For large values of n , following result is obtained.

$$\langle R_n^2 \rangle = \left[-3n + 2A \frac{2q(-1+r)^2}{2q+1-r} + \frac{128q}{4(2q+1-r)^2} \frac{n}{1-r} [1+(q-r)(1-q)] \right] \frac{1}{3} l_0^2$$

It is shown that the above result reduces to those obtained earlier by Tobolsky and Eyring. The problem of excluded volume is excluded. The Markoff chain method has been extended to semicrystalline polymers to calculate the chain dimensions. Generalisation of the 'Tobolsky and Gupta' matrix has been done to calculate the expected square of the end-to-end distance, crystallinity, amorphicity and sequence lengths for semicrystalline polymers with orientation in both the crystalline and amorphous regions.

In chapter III, the problem of phase transition between helix and random coil in polypeptide chains is

discussed. Theory of Ising model has been used to study dimensional changes during melting in normal paraffines. It is based on the cell model for diffuse transition and involves writing the Ising matrix in terms of segment pair partition functions which are either in the amorphous or in the crystalline region. The experimental data of Flory and Vrij has been used to obtain the crystallinity vs. temperature curves. The nucleation parameter σ is adjusted to give correct melting point. The dependence of transition curves on σ values is also shown and, as expected, it gets sharper for smaller values. Density as a function of temperature is also calculated and experimental and theoretical results are compared. Because of the equivalence of the crystal structures for polyethylene and N-paraffin hydrocarbon and the virtual identity of their unit cell dimensions, it is expected that the limiting melting point for N-paraffin hydrocarbon series must be coincident with the melting point for linear polyethylene of infinite chain length. This is supported by the calculations. The nucleation parameter approaches the value 5×10^{-6} , which yields correct results for polyethylene. Effect of pressure on the system is also studied. This Ising model formalism is extended to study the effect of pressure on transition. The shift in melting point as a function of pressure is evaluated and is in good agreement with the experimental results of Matsuoka. The theory of

diffuse phase transition has been applied to explain the thermal transition in three unit copolymeric system of L-Glutamic acid, L-lysine and L-alanine. Helicity vs. temperature curves are obtained at PH3 and PH8 values; they are also in good agreement with the experimental results of Morita, Simon and Blutt.

The last chapter is devoted to concluding remarks and discusses various approximations made in the present Markoff chain approach and in treating the polymeric systems as a cooperative phenomena.

CHAPTER - I

INTRODUCTION

Macromolecular chains are formed by the successive addition of monomeric units and have a threadlike structure. They consist of sequences of similar, though not necessarily identical, chemical units connected together by covalent bonds into chains which frequently contain more than ten thousand atoms. They may exist as discrete molecules or they may be interconnected in various ways giving rise, in extreme cases, to a continuous network of chains in which the concept of individual molecules loses its significance. Physical, chemical, thermodynamic and various other properties of these long chain molecules differ very much from those of the short chain and low molecular weight substances of similar composition. This is largely due to the size, shape and configuration that the polymer chain takes up. This, in turn, depends on the freedom of internal rotation around single bonds and the nature of side groups. The polymer may be either completely amorphous, semi-crystalline or highly crystalline according to the arrangement and packing of the molecular chains. The mechanical behaviour of such systems depends on the distribution and extent of crystallisation. In general, they can be classified as either natural or synthetic. In the former, we have, e.g., cellulose and proteins whereas in the latter classification are included materials like polyethylene, polypeptides and polynucleotides.

The subject matter of this thesis deals with a few problems regarding the configurational statistics, molecular

dimensions and the problem of phase transition in linear hydrocarbons (finite system) and tricopolymers of glut²⁰-lys²⁰-alan⁶⁰. The effect of pressure on the nature and transition in polyethylene is also studied.

A polymer described by a chemical formula is a mixture of a multiplicity of different configurations. These, almost infinite number of conformations in space, come about because of the presence of internal rotations about single bonds. The problem of the geometry of the polymer chain, therefore, acquires a statistical character. The statistical treatment is based on the existence of large ensembles of members possessing independent degrees of freedom. Polymer chains are in fact such ensembles. However, the totality of polymer chains, with the exception of a few, is never really an ensemble of identical objects. It is a complex mixture of entities which are heterogeneous in composition and structure. Application of statistical theory to a given system generally requires a knowledge of its energy levels. But some polymer problems can be solved without this knowledge, e.g., the state of a macromolecular system can be characterized by its dimensions and not by its total energy. Consequently, the states of the system can be regarded as states of different dimensions rather than states of different energy.

In extremely dilute solutions of polymers, the individual chain molecules are virtually isolated from one another and the thermodynamic and gross physical properties

like viscosity, light scattering, etc. of the solution depend directly on the mean configuration and free energy of a single molecule. A quantity like the expected square of the end-to-end distance $\langle R_n^2 \rangle$, where n is the number of links, of a polymer chain is important for determining the physical behaviour of polymers.

The knowledge of $\langle R_n^2 \rangle$ is important in determining light scattering data function $P(\mu)$; which, as given by Debye¹, is

$$P(\theta) = \frac{1}{N^2} \sum_{i,j=1}^N \left(\frac{\sin \mu R_{ij}}{\mu R_{ij}} \right) \quad (1-1)$$

where θ is the scattering angle, N is the number of atoms in the chain, R_{ij} is the distance between i th and j th atoms, $\mu = \frac{4\pi}{\lambda'} \sin \frac{\theta}{2}$, and λ' is the wavelength of the light in the solution. Averaging is carried out over all chain configurations. By neglecting the higher order terms, following result is obtained

$$P(\theta) = \frac{1}{N^2} \sum_{i,j} \exp \left(- \mu^2 \langle R_{ij}^2 \rangle / 6 \right) \quad (1-2)$$

The hydrodynamic properties of macromolecules in solution (viscosity, sedimentation, etc.) are determined by the dimensions of the macromolecules. For example, the viscosity of polymer solution is given by

$$\eta = \phi \frac{(\bar{R}^2)^{3/2}}{M} \quad (1-3)$$

where M is the molecular weight and ϕ is a constant. The empirical value of ϕ obtained by Flory² by treating the results of experiments in which viscosity and light scattering were measured for different polymer solvent pairs, is equal to

$$\phi = 2.1(\pm 0.2) \cdot 10^{23}$$

$$\left[\text{If } (\bar{R}^2)^{1/2} \text{ is measured in cm. and } \eta \text{ in cm}^3/\text{g} \right]$$

In this way, the above equation gives a convenient method of determining (\bar{R}^2) from the characteristic viscosity and the molecular weight.

The value of $\langle R^2 \rangle$ is also useful in determining the coefficient of translational diffusion D_t and the sedimentation constant S through the relations

$$D_t = \frac{KT}{F_t} \quad (1-4)$$

$$\text{and} \quad S = \frac{M(1-\bar{v}\rho)}{N_A F_t} \quad (1-5)$$

(\bar{v} is the partial specific volume of the polymer and ρ is the density of the solvent), F_t is the coefficient of translational friction and is related to the experimentally observed quantities. For linear chains in an ideal solvent (for which a gaussian distribution is valid)

$$F_t = P \langle R^2 \rangle^{\frac{1}{2}} n \quad (1-6)$$

where P is a constant and its value has been found to be 5.1. Hence knowing $\langle R^2 \rangle$ and other quantities, the values of S and D_t can be obtained.

Earlier, the problem of finding $\langle R^2 \rangle$ has been tackled by Eyring³, Lifson⁴, Hovee⁵ and Suzuki⁶. They have assumed that the polymers are formed by the successive addition of C-C bonds in a random manner with the only restriction that the bond angles have specified values. An account of the calculation of chain length using the method of matrix algebra has been given by Volkenstein⁷.

The properties of the polymers depend on the shapes or the configurations that the polymer chains can adopt, the flexibility of the chains, and the presence and extent of the cross-linking or branching. The idea of the "excluded volume effect" was suggested for the first time by Flory⁸ in 1949. The excluded volume arises due to the long range correlations of the chain elements. Montroll⁹, Hermans et al¹⁰, Stockmayer and Fixman¹¹, James¹², Saito¹³ and others¹⁴ have given due consideration to this 'effect' in developing their theories. Lifson¹⁵, Nagai¹⁶ and Tobolsky¹⁷ have considered the effect of branching on polymer dimensions. It is intuitively obvious that if the molecule consists of branches, the molecule is going to be more

compact than a straight chain of the same molecular weight. One can define a parameter g as the ratio between the average square length of a branched molecule and the average square length of a linear molecule.

$$g = \frac{\langle R^2 \rangle}{\langle R_0^2 \rangle} \quad (1-7)$$

In general, g is less than one if there is branching in the molecule. Lifson¹⁸ also considered the effect of charged side groups and determined the molecular dimensions for polyelectrolyte molecules.

Since the introduction by Kuhn^{19,20} of the random walk model to approximate mathematically the distributions of the configurations that flexible linear molecules might assume, the theoretical calculations of the mean dimensions of polymeric molecules has been the subject of numerous publications^{9,11,21-23} in recent years. In a random walk model, the actual molecule is replaced by an artificial one in which instead of having the molecule composed of actual bonds with fixed valence angles and a certain amount of restricted rotation, the molecule is constructed of statistical segments. It is assumed that a polymer chain is formed by the addition of successive bond vectors in such a way as if they are the successive steps of a random walk. The formalism of the mathematical method of Markoff chains has been used. Its use has been earlier demonstrated by

several other workers, e.g., Montroll²⁴, Tobolsky and Gupta²². A polymer chain can be considered as a Markoff chain because the relative orientation of a unit is dependent upon the position of the preceding one.

In the next chapter, two models based on random walks on cubic and diamond lattices are considered. In the former, a polymer chain with orientation in both crystalline and amorphous phases is studied whereas the diamond lattice model is used to approximate an oriented hydrocarbon type chain with short range correlations. A polymeric system is characterized by parameters such as expected square of the end-to-end distance, the extent of crystallisation and crystallite sizes. These parameters have been evaluated. Of the two models, diamond lattice model is a better approximation in the sense that in linear polymeric chains such as hydrocarbons the valence C-C bond angles are the same as in a diamond lattice.

The third chapter is devoted to a study of order-disorder transition in macromolecular systems. Transitions in finite and infinite systems such as n-paraffins and polyethylene respectively are derived. In the latter case, the effect of pressure on transition is discussed. The Ising model approach is used and is modified to explain helix-coil transitions in a tricopolymeric system also. Order-disorder phenomenon and accompanying phase transitions have attracted physicists for a long time. They are of special interest in the case

of biopolymeric chains because the translation and transcription of the genetic information is closely related to the uncoiling of a DNA molecule. In tricopolymeric systems, it was observed experimentally by Doty et al²⁵ that some physical properties like the intrinsic viscosity and optical rotation, etc. underwent considerable change on changing the conditions like the temperature and solvent composition. This change in the properties due to change in such physical conditions was correlated to the change from helical structure to a random coil structure. This phenomenon is known as the "helix-coil transition". As the transition is quite sharp, it is referred to as a phase transition of the first order because of the accompanied changes in the entropy of the system.

Several attempts have been made to theoretically interpret this helix-coil transition and they are all based on a modification of the Ising model proposed for ferromagnetism. It has been studied by Zimm and Bragg²⁶, Gibbs and Di Marzio²⁷, Rice and Wada²⁸, Lifson and Roig²⁹, Hill³⁰ and others³¹. Just as a linear Ising chain is made up of two spin states defined as 'up' and 'down', so is a polymeric system made up of 'helix' and 'coil' states or 'ordered' and 'disordered' states. The aim is to evaluate the total partition function for the entire chain in terms of contributions made by individual segments. Other thermodynamic properties can be obtained from a knowledge of the

grand partition function. It has been shown by Landau and Lifshitz³² that a one-dimensional system cannot exhibit phase transition; however, experimentally it is seen that polymeric systems do exhibit what may be called a phase transition. The contradiction arises because of the assumptions made by the above authors in their theoretical approach. The assumptions are

- (a) the interaction has a finite range, and
- (b) the interaction is non-singular, i.e., of finite strength.

Once these constraints are lifted, the one-dimensional system shows all characteristics of a phase transition. The cooperative nature of hydrogen bonding in biopolymeric systems takes care of the first restriction and the introduction of a nucleation parameter which is a measure of difficulty of transition from the random coil to the helical phase in a way introduces singularity in the nearest neighbour interaction. The sharpness of the transition is governed by the magnitude of this parameter. It becomes more and more step like for decreasing values. Baker³³ has also shown that a one-dimensional system will approach even a second order transition in the limit that the range of its interaction becomes infinite. The nature of the transition also depends on the presence of the defects and size and distribution of ordered regions. The width of transition for finite system is, in general, more than that for infinite ones.

N-paraffins with finite degree of polymerisation and linear polyethylene with almost infinite chain length belong to a different class of polymers. Eventhough it is difficult in these cases to define cooperativity factors as precisely as in hydrogen bonded biopolymers, one could still use the formalism of Ising model. The heat of transition in such cases would reflect both intermolecular and intramolecular interactions and this in a way also takes care of the three-dimensional structure eventhough the model used is a one-dimensional one. Because of the equivalence of the crystal structures for polyethylene and N-paraffin hydrocarbon and the virtual identity of their unit cell dimensions, it is expected that the limiting melting point for N-paraffin hydrocarbon series must be coincident with the melting point for linear polyethylene of infinite chain length. This is supported by the calculations. The nucleation parameter approaches a value which is approximately the same as for polyethylene. This problem has also been studied by Flory and Vrij³⁴, Broadhurst³⁵ and others³⁶. Flory's treatment is based on the supposition that both the enthalpy and the entropy of fusion may be adequately represented by linear expressions, each comprising a term proportional to n and an additive constant for contributions associated with the end groups. The melting point T_m is expected on this basis to be related to the chain length

n as

$$T_m = \Delta H(n+a) / \Delta S(n+b) = T_m (n+a)/(n+b) \quad (1-8)$$

where ΔH and ΔS represent, respectively, the enthalpy and entropy of melting per CH_2 group in the limit $n \rightarrow \infty$, and $a\Delta H$ and $b\Delta S$ are the end-group contributions. It is to be noted, however, that T_m and other parameters appearing in equation (1-8) as well, will depend, in general, on temperature and should not, on the basis set forth above for this equation, be treated as constants. Revisions appropriately taking account of the dependence of T_m on temperature were introduced by Broadhurst³⁵. His analysis retains, however, the basic assumption of linearity of the enthalpy and of the entropy with n at constant temperature.

Lastly, a part of Chapter III is devoted to a study of pressure on the transition curve. The mechanical behaviour and morphological structures of a polymeric material are markedly changed when subjected to stress, e.g., vulcanised rubber which does not crystallize at ordinary temperature becomes highly crystalline when subjected to tension. Further the elongation of a network polymer in the amorphous state increases its free energy and if the polymer is capable of crystallising, its melting point will also be increased. The effect of strain on melting point has been theoretically studied by Flory³⁷. His model consists of

bundle like crystallites with the direction of the chain through the crystallite being perfectly aligned along the drawing direction. Furthermore, the exit from one crystallite, and the entrance into the next, was assumed to occur in the manner which minimized the path of the intervening amorphous chain. These conditions imply that the sample is rather well drawn prior to crystallization. The equilibrium degree of crystallinity, ω , for any temperature T was found by letting $(\partial F / \partial \omega)_{T,p}$ vanish, and the melting temperature T_m was obtained from this relation by setting $\omega = 0$. This model is somewhat oversimplified because it fails for small strains as the assumption of perfect alignment is no longer valid. In the present approach, the formalism of Ising model in a magnetic field has been used. The relative contribution of a segment in a crystalline state with respect to one in the amorphous state is changed due to applied pressure and this is built into the Ising matrix. The theory of cooperative phenomenon is used.

The last chapter is the concluding part of the thesis. Here, a brief comparison of various approaches, limitations of the underlying assumptions and their effect on the results obtained are discussed. Suggestions for further work and improvement are made.

REFERENCES

1. P. Debye, J. Phys. & Colloid Chem. 51, 18 (1947).
2. P.J. Flory, Principles of Polymer Chemistry, Cornell, Ithaca, 1953.
3. H. Eyring, Phys. Rev. 39, 746 (1932).
4. S. Lifson, J. Chem. Phys. 29, 80 (1958); 30, 964 (1959).
5. C.A. Hoeve, J. Chem. Phys. 32, 888 (1960).
6. Y. Suzuki, J. Chem. Phys. 34, 79 (1961).
7. M.V. Volkenstein, J. Poly. Sc. 29, 441 (1958).
8. P.J. Flory, J. Chem. Phys. 18, 103 (1949).
9. E.W. Montroll, J. Chem. Phys. 18, 734 (1950).
10. J.J. Hermans, M.S. Klamkin and R. Ullman, J. Chem. Phys. 20, 1360 (1952).
11. B.H. Zimm, W.H. Stockmayer and M. Fixman, J. Chem. Phys. 21, 1721 (1953).
12. H.M. James, J. Chem. Phys. 21, 1628 (1953).
13. N. Saito, J. Phys. Soc. Japan 9, 780 (1954).
14. F. Bueche, J. Chem. Phys. 21, 205 (1953).
15. S. Lifson, J. Chem. Phys. 29, 80 (1958); 30, 964 (1959).
16. K. Nagai, J. Chem. Phys. 30, 660 (1959).
17. A.V. Tobolsky, J. Chem. Phys. 31, 387 (1959).
18. S. Lifson, J. Chem. Phys. 29, 89 (1958).
19. W. Kuhn, Kolloid Z. 68, 2 (1934).
20. W. Kuhn, Kolloid Z. 101, 248 (1942).
21. R. Ullman and J.J. Hermans, J. Poly. Sc. 10, 559 (1953).
22. A.V. Tobolsky and V.D. Gupta, J. Chem. Phys. 36, 1999 (1962).

23. F.T. Wall, S. Windwar and P.J. Gans, J. Chem. Phys. 37, 1461 (1962).
24. E.W. Montroll, J. Chem. Phys. 18, 734 (1950).
25. P. Doty, A.M. Holtzer, J.H. Bradbury and E.R. Blout, J. Am. Chem. Soc. 76, 4493 (1954).
P. Doty and J.T. Yang, *ibid* 78, 498 (1956).
P. Doty, J.H. Bradbury and A.M. Holtzer, *ibid*, 78, 947 (1956).
26. B.H. Zimm and J.K. Bragg, J. Chem. Phys. 31, 526 (1959).
27. J.H. Gibbs and E.A. Di Marzio, J. Chem. Phys. 30, 271 (1959).
28. S.A. Rice and A. Wada, J. Chem. Phys. 29, 233 (1958).
29. S. Lifson and A. Roig, J. Chem. Phys. 34, 1963 (1961).
30. T.L. Hill, J. Chem. Phys. 30, 383 (1959).
31. L. Peller, J. Phys. Chem. 63, 1194 (1959).
32. J. Applequist, J. Chem. Phys. 38, 934 (1963).
K. Nagai, J. Phys. Soc. Japan 15, 407 (1960).
L. Landau and E. Lifshitz, Statistical Physics, Pergamon Press (1966).
33. G.A. Baker, Jr., Phys. Rev. 122, 1477 (1961).
34. P.J. Flory and A. Vrij, J. Am. Chem. Soc. 85, 3548 (1963).
35. M.G. Broadhurst, J. of Research of the National Bureau of Standards—A Physics and Chemistry 70A, 481 (1966).
36. W.E. Garner, K. Van Bibber and A.M. King, J. Chem. Soc. 1533 (1931).
37. P.J. Flory, J. Chem. Phys. 15, 397 (1947).

CHAPTER - II

MOLECULAR DIMENSIONS IN SEMICRYSTALLINE AND
ORIENTED CHAINS

2.1 INTRODUCTION

As discussed briefly in the first chapter, one of the parameters characterising a macromolecular chain is the expected square of the end-to-end distance $\langle R_n^2 \rangle$, where n is the number of links. This distance is important in developing the equation of state for rubber elasticity, for deriving equations expressing intrinsic viscosity in terms of the chain length, for interpreting light scattering data from dilute solutions and for promoting the growth of other important theoretical concepts. Various methods have been used for its calculation depending on the geometry of the molecule.

In this chapter, Markoff chain method has been developed to derive explicit formulas for the n step transition probabilities p_{mn}^k which are used in the calculations of the expected square of the end-to-end distance for a polymer chain.

2.2 MARKOFF CHAIN METHOD

In the theory of Markoff chains, the simplest generalization is that the outcome of any event depends on the outcome of the directly preceding event (and only on it). In the present problem of the calculation of molecular dimensions

of the polymer chains, the above-mentioned generalization has been imposed on the random walk model so that Markoff chain method can be applied to it. As comprehensive reviews of this method are available in literature^{1,2}, only a brief account of this method is presented here for the sake of completeness.

Let a Markoff chain be designated in terms of a set of dependent variables Z_0, Z_1, Z_2, \dots , and let these variables be related so that the probability distribution of Z_j ($j = 0, 1, 2, \dots$) is uniquely defined by that of Z_{j-1} and the law of dependence is independent of j .

Let the possible values of Z_j be a_1, a_2, \dots, a_M . Then the probability distribution of Z_j is defined by

$$p_m(j) = \text{pr}(Z_j = a_m) \quad m = 1, 2, \dots, N$$

$$\text{and } j = 0, 1, 2, \dots \quad (2-1)$$

(Here the common notations of the theory of probability have been used and the symbol $\text{pr}(Z_j = a_m)$ denotes the probability that Z_j equals a_m .)

As Z_j can take one of the values from the set a_1, a_2, \dots, a_N , we know

$$\sum_{m=1}^N p_m(j) = 1 \quad \text{for all } j \quad (2-2)$$

A simple Markoff chain can be completely characterized in terms of the initial probability distribution of Z_0 , i.e., $p_m(0)$ and the N^2 transition probabilities p_{mn}

$$p(n \rightarrow m) = p_{mn} = \text{pr}(Z_{j+1} = a_m \text{ if } Z_j = a_n) \quad (2-3)$$

$$p_{mn} \geq 0 \quad \text{if} \quad 1 \leq n, \quad m \leq N$$

Since $Z_j = a_n$ implies with certainty that Z_{j+1} has one of the values a_1, a_2, \dots, a_N , we have

$$\sum_{m=1}^N p_{mn} = 1 \quad \text{for } n = 1, 2, \dots, N \quad (2-4)$$

The probability of the simultaneous occurrence of two linked events is equal to the product of the unconditional probability of the occurrence of one of the events and conditional probability of the other assuming that the first event has occurred. Hence

$$\text{pr}(Z_{j+1} = a_m \text{ and } Z_j = a_n) = p_{mn} p_n(j) \quad (2-5)$$

Since the probability of occurrence of a given event is the sum of the probabilities of mutually independent ways in which it can happen,

$$p_m(j+1) = \sum_{n=1}^N p_{mn} p_n(j) \quad \text{for } m=1, \dots, N \text{ and } j = 0, 1, \dots \quad \dots (2-6)$$

Similarly the distribution of Z_{j+2} is obtained by iteration of (2-6), as follows

$$\begin{aligned} p_m(j+2) &= \sum_{n=1}^N p_{mn} p_n(j+1) \\ &= \sum_{n_2=1}^N \left(\sum_{n_1=1}^N p_{mn_1} p_{n_1 n_2} \right) p_{n_2}(j) \end{aligned} \quad (2-7)$$

In general

$$p_m(j+k) = \sum_{n_1=1}^N \sum_{n_2=1}^N \dots \sum_{n_k=1}^N p_{mn_1} p_{n_1 n_2} \dots p_{n_{k-1} n_k} p_{n_k}(j) \quad \dots(2-8)$$

Hence $p_m(k)$ can be calculated from initial distribution $p_m(o)$ [when $j=o$] by application of equations (2-7) and (2-8).

This multiple summation process can be avoided by writing these relations in a matrix form. The transition probabilities p_{mn} can thus be arranged in a matrix of transition probabilities,

$$P = \begin{bmatrix} p_{11} & p_{12} & p_{13} & \dots & p_{1N} \\ p_{21} & p_{22} & p_{23} & \dots & \\ p_{31} & p_{32} & p_{33} & \dots & \\ \vdots & & & & \\ p_{N1} & p_{N2} & p_{N3} & \dots & p_{NN} \end{bmatrix} \quad (2-9)$$

where the first subscript stands for row and the second for column.

P is a square matrix which has non-negative elements and the sum of all the elements in a row is unity. Such a matrix (finite or infinite) is called a stochastic matrix. Any stochastic matrix can be used as a matrix of transition probabilities and with initial distribution $\{p_m(o)\}$ it

completely defines a Markoff chain.

Let $\underline{X}_1, \dots, \underline{X}_N$ be the set of row vectors, $\underline{Y}_1, \dots, \underline{Y}_N$ be the set of column vectors, $\lambda_1, \dots, \lambda_N$ be the corresponding eigenvalues of the matrix P. These quantities satisfy the equations

$$\underline{X}_k P = \lambda_k \underline{X}_k \quad \text{and} \quad P \underline{Y}_k = \lambda_k \underline{Y}_k \quad (2-10)$$

p_{mn}^k is the kth step transition probability from the state m to n. These elements can be evaluated from the following relation

$$p_{mn}^k = \sum_{r=1}^N C_r^{-1} \lambda_r^k X_r^{(m)} Y_r^{(n)} \quad (2-11)$$

C_r^{-1} is the inverse of the inner product of row and column vectors.

2.3 EXPECTED SQUARE OF THE END-TO-END DISTANCE

Consider the freely rotating segments of a chain to be each resolved into three components of length $l/\sqrt{3}$ along X, Y, Z axes. These are called link vectors. Let a chain of n links be represented by vectors $(X^{(i)}, Y^{(i)}, Z^{(i)})$, $i = 0, 1, 2, \dots, n-1$. The expected square of the end-to-end distance is denoted by

$$\begin{aligned} \langle R_n^2 \rangle = E [& (X^{(0)} + X^{(1)} + \dots + X^{(n-1)})^2 \\ & + (Y^{(0)} + Y^{(1)} + \dots + Y^{(n-1)})^2 \\ & + (Z^{(0)} + Z^{(1)} + \dots + Z^{(n-1)})^2] \end{aligned} \quad (2-12)$$

$$\begin{aligned}
&= 3n+2 \sum_{i=0}^{n-2} \sum_{j=i+1}^{n-1} E [X^{(i)} X^{(j)} + Y^{(i)} Y^{(j)} + Z^{(i)} Z^{(j)}] \\
&= 3n+2 \sum_{i=0}^{n-2} \sum_{k=1}^{n-1-i} E [X^{(0)} X^{(k)} + Y^{(0)} Y^{(k)} + Z^{(0)} Z^{(k)}] \quad (2-13)
\end{aligned}$$

Substituting

$$L_k = E [X^{(0)} X^{(k)} + Y^{(0)} Y^{(k)} + Z^{(0)} Z^{(k)}] \quad (2-14)$$

We get,

$$\begin{aligned}
\langle R_n^2 \rangle &= 3n + 2 \sum_{i=0}^{n-2} \sum_{k=1}^{n-1-i} L_k \\
&= -3n + 2 \sum_{i=0}^{n-1} \sum_{k=0}^{n-1-i} L_k \quad (2-15)
\end{aligned}$$

There can be large number of configurations which a molecular system can assume. Therefore, one has to apply a statistical approach. It is convenient to replace the actual molecule with a synthetic one in which the actual chemical bonds are replaced by artificial ones. Instead of having the molecule composed of actual bonds with fixed valence angles and a certain amount of restricted rotation, the molecule is constructed of statistical segments. These are chosen such that the average square length of synthetic molecule is the same as the average square length of the real molecule. For this purpose, models are chosen which are nearest to the structure of actual molecular system.

To calculate the molecular dimensions of polymer chains, two types of models are considered. In the first, the polymer chain traces out a path on a cubic lattice (Figure 1) and in the second, the polymer chain traces out a path on a diamond lattice (Figure 2). In the former, the general problem of molecular dimensions in a semi-crystalline polymer chain with orientation in both ordered and disordered phases is considered, whereas in the latter, the conformational statistics of an oriented hydrocarbon type chain with short range interactions is studied.

2.4 CUBIC LATTICE MODEL WITH ORIENTATION IN AMORPHOUS AND CRYSTALLINE PHASES

Real polymer chains consist of amorphous and crystalline regions. The sequences of segments in these regions can be represented as

r r r h h r h h r h h r h h r

where r corresponds to a segment in the amorphous region and h that in the crystalline region. Let us assume that the semicrystalline polymer chain under consideration traces out a path on a cubic crystal lattice such that the crystalline and amorphous regions of the chain have preferred directions only along $\pm x$, $\pm y$ and $\pm z$ axes. Each segment consists of three links pointing successively in the three preferred directions.

A $\pm x$ crystalline region is one in which the chain progresses in the $\pm x$ direction but in which the y and z

—— BOND IN THE CRYSTALLINE REGION

---- BOND IN THE AMORPHOUS REGION.

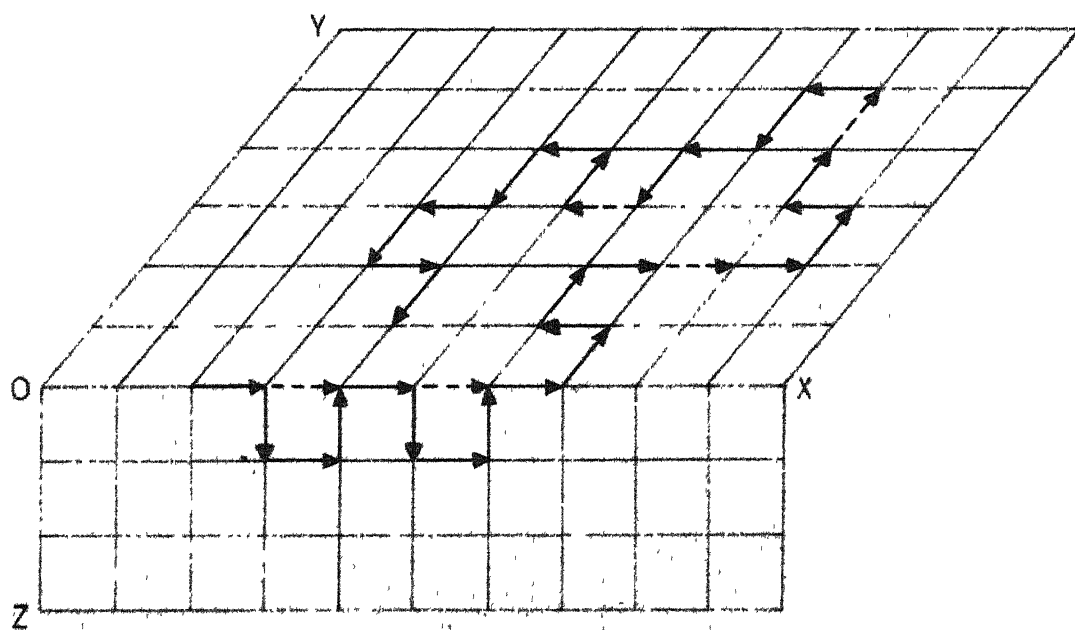


FIG.1. POLYMER CHAIN ON A CUBIC LATTICE.

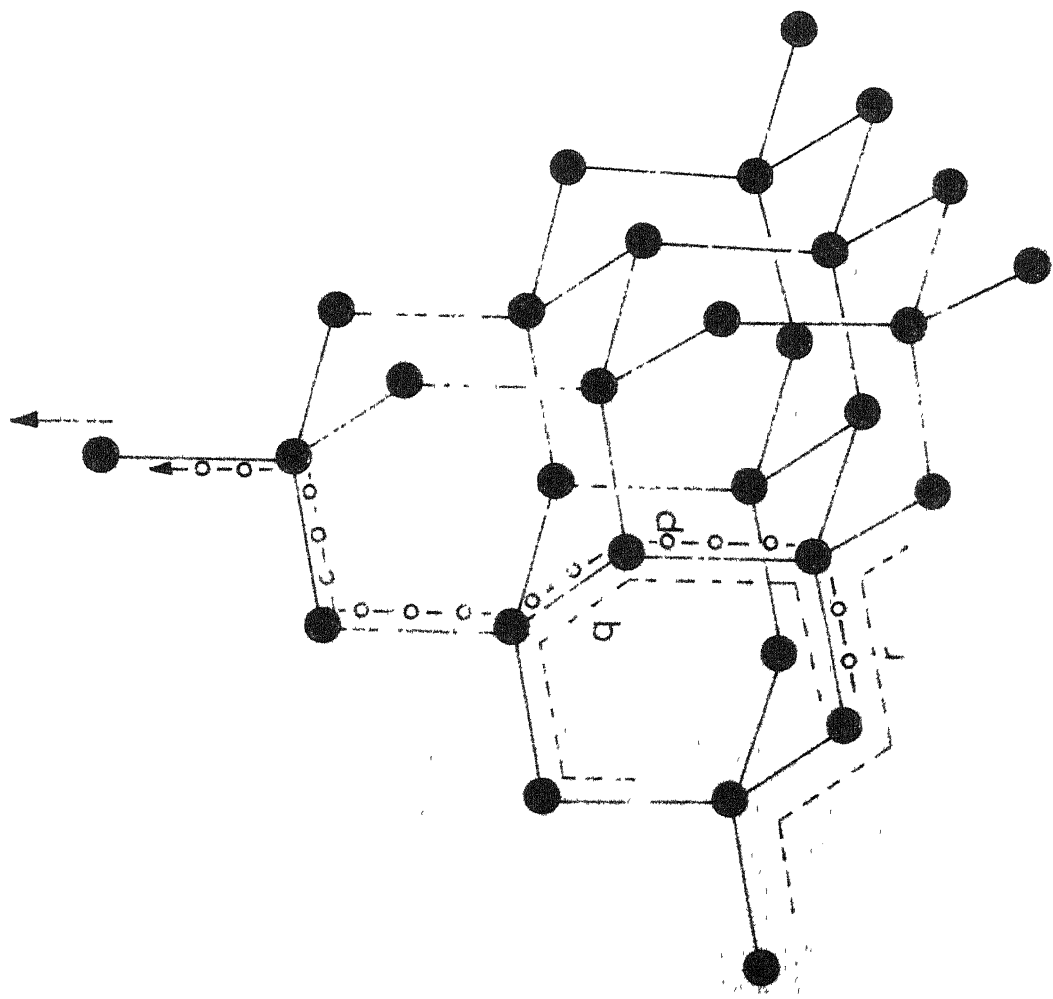


FIG. 2. HYDROCARBON TYPE CHAIN ON DIAMOND LATTICE

vectors are symmetrically spiralled so that the net contribution of the y and z chain components over this entire region is zero. Similar discussions are applicable for crystals in the other five possible directions. If the bond length or the length of a segment is taken to be l_0 , then the length of each link in the amorphous or crystalline regions will be $l_0/\sqrt{3}$. But for simplicity this length is taken to be unity in calculations and the factor $l_0/\sqrt{3}$ is again introduced at the end of calculations.

The succession of $\pm x$ links (i.e., every third link) of the polymer chain forms a Markoff chain. Consider the elements of a chain to have five possible states r_+ , r_- , h_+ , h_- and h_0 . The state r_+ denotes an x link in the amorphous region pointing in the $+x$ direction, r_- denotes an x link in the amorphous region pointing in the $-x$ direction, h_+ denotes an x link in a $+x$ crystalline region, h_- denotes an x link in a $-x$ crystalline region, h_0 denotes an x link in a $\pm y$ or $\pm z$ crystalline region (the average length of such a link is zero).

Tobolsky and Gupta³ have treated the sequence of x links by Markoff chain method taking into account the orientation only in the crystalline region. They have used the following transition probability matrix for describing the succession of states,

$$\begin{array}{c}
 r_+ \quad r_- \quad h_+ \quad h_- \quad h_o \\
 P = \begin{array}{c} h_+ \\ h_- \\ h_o \end{array} \left[\begin{array}{ccccc}
 \frac{1}{2}(1-p) & \frac{1}{2}(1-p) & \beta_x p & 0 & (1-\beta_x)p \\
 \frac{1}{2}(1-p) & \frac{1}{2}(1-p) & 0 & \beta_x p & (1-\beta_x)p \\
 1-\alpha & 0 & \alpha & 0 & 0 \\
 0 & 1-\alpha & 0 & \alpha & 0 \\
 \frac{1}{2}(1-\alpha) & \frac{1}{2}(1-\alpha) & 0 & 0 & \alpha
 \end{array} \right] \quad (2-16)
 \end{array}$$

where the parameter p represents the probability that a bond in an amorphous region will be followed by a bond in crystalline region, the quantity α is the probability that a bond in a crystalline region is followed by another bond in the same crystalline region and the factor β_x is the fraction of crystallites oriented in the $+x$ direction. Similarly β_y and β_z are the fraction of crystallites oriented in the $+y$ and $+z$ direction respectively. Therefore,

$$\beta_x + \beta_y + \beta_z = 1 \quad (2-17)$$

For an unoriented crystalline polymer,

$$\beta_x = \beta_y = \beta_z = 1/3 \quad (2-18)$$

and for complete orientation in the x direction,

$$\beta_x = 1, \quad \beta_y = \beta_z = 0 \quad (2-19)$$

Tobolsky and Gupta³ have further calculated the expected square of the end-to-end distance projected along the x , y

and z directions, average sequence length in the crystalline and amorphous regions, fractional crystallinity and fractional amorphicity using the Markoff chain method. All these results were derived for a chain of n links in each of the three directions, i.e., for a chain of n bonds. These results are given below. The expected square of the end-to-end distance in the x direction, $\langle R_x^2 \rangle$ for n links

$$\langle R_x^2 \rangle = n \left[\frac{1-\alpha + \beta_x p}{1-\alpha + p} \cdot \frac{1+p \beta_x}{1-p \beta_x} + \frac{2p \beta_x (2-\alpha)}{(1-p \beta_x)(1-\alpha)(1-\alpha+p)} \right] \frac{1}{3} \quad \dots(2-20)$$

Similar expressions with β_y and β_z can be written for

$$\langle R_y^2 \rangle \text{ and } \langle R_z^2 \rangle .$$

The sequence length in the amorphous region
(uninterrupted by r_+ or r_- states)

$$= 1/(1-\alpha) \quad (2-21)$$

The sequence length in the amorphous region (uninterrupted
by h_+ or h_- states)

$$= 1/p \quad (2-22)$$

$$\text{Fractional crystallinity} = p/(1-\alpha+p) \quad (2-23)$$

$$\text{Fractional amorphicity} = (1-\alpha)/(1-\alpha+p) \quad (2-24)$$

Here the orientation in the amorphous region is not considered. However, there are polymers which show orientation in amorphous region also as has been experimentally

observed in X-ray studies⁴ in samples such as polyethylene.

In the present work Tobolsky and Gupta's³ work has been further extended by including the orientation in the amorphous region also. Now the transition probability matrix is given as

$$P = \begin{matrix} & \begin{matrix} r_+ & r_- & h_+ & h_- & h_o \end{matrix} \\ \begin{matrix} r_+ \\ r_- \\ h_+ \\ h_- \\ h_o \end{matrix} & \begin{bmatrix} \mu & 1-p-\mu & \beta p & 0 & (1-\beta)p \\ (1-p-\mu) & \mu & 0 & \beta p & (1-\beta)p \\ (1-\alpha) & 0 & \alpha & 0 & 0 \\ 0 & (1-\alpha) & 0 & \alpha & 0 \\ (1-\alpha)/2 & (1-\alpha)/2 & 0 & 0 & \alpha \end{bmatrix} \end{matrix} \quad (2-25)$$

Here an extra parameter μ is introduced, which denotes the orientation in the amorphous region. To calculate the molecular dimensions Markoff chain method has been used and only those components are considered which are in the $\pm x$ direction. If the length of the successive vectors be $x^{(0)}, x^{(1)}, x^{(2)}, \dots, x^{(n-1)}$, then the expected square of the end-to-end distance is given by

$$\langle R_x^2 \rangle = [x^{(0)} + \dots + x^{(n-1)}]^2 \quad (2-26)$$

$$= \sum_{i=0}^{n-1} x^{(i)} x^{(i)} + 2 \sum_{i=0}^{n-2} \sum_{j=i+1}^{n-1} x^{(i)} x^{(j)} \quad \dots (2-27)$$

$$= nE(\pm 1) + 2 \sum_{k=1}^{n-1} (n-k) L_k \quad (2-28)$$

where $E(\pm 1)$ is the expectation that an x vector has the value ± 1 rather than zero and $L_k = E(x^{(c)} x^{(k)})$.

In the Markoff formalism the value of L_k can be written as

$$L_k = p_{11}^k - p_{12}^k + p_{13}^k - p_{14}^k \quad (2-29)$$

where p_{11}^k, p_{12}^k , etc., are the elements in the first row of the k th power of P and it is assumed that the chain started in the r_+ state.

The chain can start in any of the five possible states, i.e., r_+, r_-, h_+, h_- or h_0 . The growth of the chain will depend on its initial starting state. The end-to-end distance is calculated for the chain starting in each one of the five states separately and are weighted according to the respective steady state probabilities. They are finally combined to get $\langle R_x^2 \rangle$. Using the notation 1,2,3,4,5 for r_+, r_-, h_+, h_- and h_0 respectively, we have

$$\langle R_x^2 \rangle = \sum_{i=1}^5 \langle R_{x_i}^2 \rangle \quad (2-30)$$

2.5 STATIONARY STATE PROBABILITY

When N is sufficiently large the system eventually attains a steady state and there is a finite probability called stationary state probability, of its being found in any one of the available states irrespective of the initial state. In statistical mechanics this corresponds

to the system which has attained equilibrium; i.e., there is no further time development of the system. These stationary state probabilities would then be the normalised components of the eigenvector corresponding to eigenvalue, $\lambda = 1$.

The stationary state probabilities p are given by the relations $mP = m$ and the stochastic property $\sum_i p_{ij} = 1$.

$$p = \frac{1-\alpha}{2(1-\alpha+p)} \quad \text{for } r_+ \text{ and } r_- \text{ states} \quad (2-31a)$$

$$= \frac{\beta p}{2(1-\alpha+p)} \quad \text{for } h_+ \text{ and } h_- \text{ states} \quad (2-31b)$$

$$= \frac{p(1-\beta_1)}{(1-\alpha+p)} \quad \text{for } h_0 \text{ state} \quad (2-31c)$$

From these

$$E(\pm 1) = \frac{(1-\alpha + \beta p)}{1-\alpha+p} \quad (2-32)$$

Hence from equation (2-28)

$$\langle R_{x_1}^2 \rangle = \frac{1-\alpha}{2(1-\alpha+p)} \left[n \frac{1-\alpha + \beta p}{1-\alpha+p} + 2 \sum_{k=0}^{n-1} (n-k) L_k \right] \quad (2-33)$$

Similar expressions can be written for the other states. The problem thus reduces to the evaluation of L_k which involves the k th-step transition probabilities which, in turn, can be obtained with the help of equation (2-11).

The matrix of transition probabilities has eigenvalues $1, \alpha, \alpha-p, \lambda'$ and λ'' , where λ' and λ'' are given by

$$\lambda' + \lambda'' = \alpha + 2\mu - 1 + p$$

$$\lambda' - \lambda'' = -p (\beta - \alpha - \alpha\beta) + \alpha (2\mu - 1)$$

The various terms of p_{mn}^k are

$$p_{11}^k = p_{22}^k = \frac{1}{2(1-\alpha+p)} + \frac{\Delta \lambda^{k+1} - \alpha \Delta \lambda^k}{2 \Delta \lambda} \quad (2-34a)$$

$$p_{12}^k = p_{21}^k = \frac{1}{2(1-\alpha+p)} - \frac{\Delta \lambda^{k+1} - \alpha \Delta \lambda^k}{2 \Delta \lambda} \quad (2-34b)$$

$$p_{13}^k = p_{24}^k = \frac{\beta p 1'}{2(1-\alpha+p)} + \frac{\beta p}{2 \Delta \lambda} \Delta \lambda^k \quad (2-34c)$$

$$p_{14}^k = p_{23}^k = \frac{\beta p 1'}{2(1-\alpha+p)} - \frac{\beta p}{2 \Delta \lambda} \Delta \lambda^k \quad (2-34d)$$

$$p_{15}^k = p_{25}^k = \frac{(1-\beta) p 1'}{(1-\alpha+p)} \quad (2-34e)$$

$$p_{31}^k = p_{42}^k = \frac{(1-\alpha) 1'}{2(1-\alpha+p)} + \frac{(1-\alpha)}{2 \Delta \lambda} \Delta \lambda^k \quad (2-34f)$$

$$p_{32}^k = p_{41}^k = \frac{(1-\alpha) 1'}{2(1-\alpha+p)} - \frac{(1-\alpha)}{2 \Delta \lambda} \Delta \lambda^k \quad (2-34g)$$

$$p_{33}^k = p_{44}^k = \frac{\beta 1''}{2(1-\alpha+p)} + \frac{(1-\beta)}{2} \alpha^k + \frac{\alpha \Delta \lambda^k - \lambda_4 \lambda_5 \Delta \lambda^{k-1}}{2 \Delta \lambda} \quad \dots (2-34h)$$

$$p_{34}^k = p_{43}^k = \frac{\beta 1''}{2(1-\alpha+p)} + \frac{(1-\beta)}{2} \alpha^k - \frac{\alpha \Delta \lambda^k - \lambda_4 \lambda_5 \Delta \lambda^{k-1}}{2 \Delta \lambda} \quad \dots (2-34i)$$

where $1 = (1-\alpha) + p(\alpha - p)^k$

$$1' = 1 - (\alpha - p)^k$$

$$1'' = p + (1-\alpha) (\alpha - p)^k$$

and Δ is the operator for $\lambda' - \lambda''$.

Substituting equations (2-34a - d) in equation (2-29),

$$L_{1k} = \frac{1}{R} (D \lambda^{k+1} + (\beta p - \alpha) D \lambda^k) \quad (2-35)$$

Making use of the following equations,

$$\sum_{k=1}^{n-1} (n-k) \lambda^k = \frac{n\lambda}{(1-\lambda)} + \frac{\lambda^{n+2}}{(1-\lambda)^2} - \frac{\lambda^2}{(1-\lambda)^2} \quad (2-36)$$

$$\frac{D\lambda}{1-\lambda} = \frac{D\lambda}{(1-\alpha)(2-2\mu-p-\beta p)} \quad (2-37)$$

$$\frac{D \lambda^2}{1-\lambda} = \frac{D \lambda (\alpha + 2\mu - 1 + p) + p(\beta - \alpha - \alpha\beta) - \alpha(2\mu - 1)}{(1-\alpha)(2-2\mu-\beta p) - p} \quad (2-38)$$

and retaining only the leading terms, one gets

$$\sum_{k=1}^{n-1} (n-k) L_{1k} = \frac{n [(1-\alpha)(2\mu+p-1) + \beta p(2-\alpha)]}{(1-\alpha)(2-2\mu-p-\beta p)} \quad (2-39)$$

In the manner outlined above, it can be easily seen that

$$\langle R_{x_2}^2 \rangle = \langle R_{x_1}^2 \rangle \quad (2-40)$$

$$\langle R_{x_3}^2 \rangle = \langle R_{x_4}^2 \rangle = \frac{\beta p n}{2(1-\alpha+p)} \left[\frac{(1-\alpha+\beta p)}{(1-\alpha+p)} + \frac{2 [1 + \beta p(1-\alpha) - \alpha(2\mu-1+p)]}{(1-\alpha)(2-2\mu-p-\beta p)} \right] \dots (2-41)$$

$$\langle R_{x_5}^2 \rangle = \frac{(1-\beta)}{(1-\alpha+p)} \frac{1-\alpha+\beta p}{1-\alpha+p} n \quad (2-42)$$

Thus, finally, from equation (2-30)

$$\langle R_x^2 \rangle = n \left[\frac{1-\alpha + \beta p}{1-\alpha + p} \frac{(2-2\mu - p + \beta p)}{(2-2\mu - p - \beta p)} + \frac{2\beta p (2-\alpha)}{(1-\alpha)(1-\alpha+p)(2-2\mu-p-\beta p)} + \frac{2(p+2\mu-1)[(1-\alpha)^2 - \alpha\beta p]}{(1-\alpha+p)(2-2\mu-p-\beta p)(1-\alpha)} \right] \frac{1}{3} \quad \dots(2-43)$$

Similar expressions can be written for $\langle R_y^2 \rangle$ and $\langle R_z^2 \rangle$.

2.6 FRACTIONAL CRYSTALLINITY AND AMORPHICITY

The fraction of x components which exist in the h_+ , h_- and h_0 states can be regarded as the fractional degree of crystallinity and is given by

$$\lim_{k \rightarrow \infty} (p_{13}^k + p_{14}^k + p_{15}^k) = \frac{p}{(1-\alpha+p)} \quad (2-44)$$

Similarly the fractional degree of amorphicity is given by

$$\lim_{k \rightarrow \infty} (p_{11}^k + p_{12}^k) = \frac{(1-\alpha)}{(1-\alpha+p)} \quad (2-45)$$

2.7 SEQUENCE LENGTHS IN CRYSTALLINE AND AMORPHOUS REGIONS

The probability that a vector continues in the crystalline + or - state over (n-1) steps is α^{n-1} and that it gets out in the nth step is $(1-\alpha)$. Hence sequence length in the crystalline state is

$$\lim_{n \rightarrow \infty} \sum n(1-\alpha) \alpha^{n-1} = \frac{1}{(1-\alpha)} \quad (2-46)$$

Similarly, sequence length in the amorphous region (uninterrupted by crystalline states)

$$= 1/p \quad (2-47)$$

By substituting $\mu = \frac{1-p}{2}$, the results of Tobolsky and Gupta³ can be obtained.

2.8 DIAMOND LATTICE MODEL FOR A HYDROCARBON TYPE CHAIN WITH SHORT-RANGE CORRELATIONS

Now consider that the polymer chain traces out a path on a diamond lattice. This lattice is a better approximation than a cubic lattice in the sense that in some polymeric chains such as linear hydrocarbon type, the valence C-C bond angles are the same as in a diamond lattice. Various polymers have such bonds, for example a polymer like polyethylene has isomers⁵ shown in Figure 3. In a diamond lattice each lattice point is joined to its four nearest neighbours through tetrahedral bonds (Figure 4a) and, therefore, each carbon atom has four such vectors ending on it. The aim here is to find a set of axes which can describe these bonds in a convenient way. For this an orthogonal set of axes is chosen and the points A, B, C, D are defined by (0,0,0), (2,2,0), (0,2,2), (2,0,2). Joining these points gives a tetrahedron thereby allowing us to label A, B, C, D as atoms (Figure 4a).

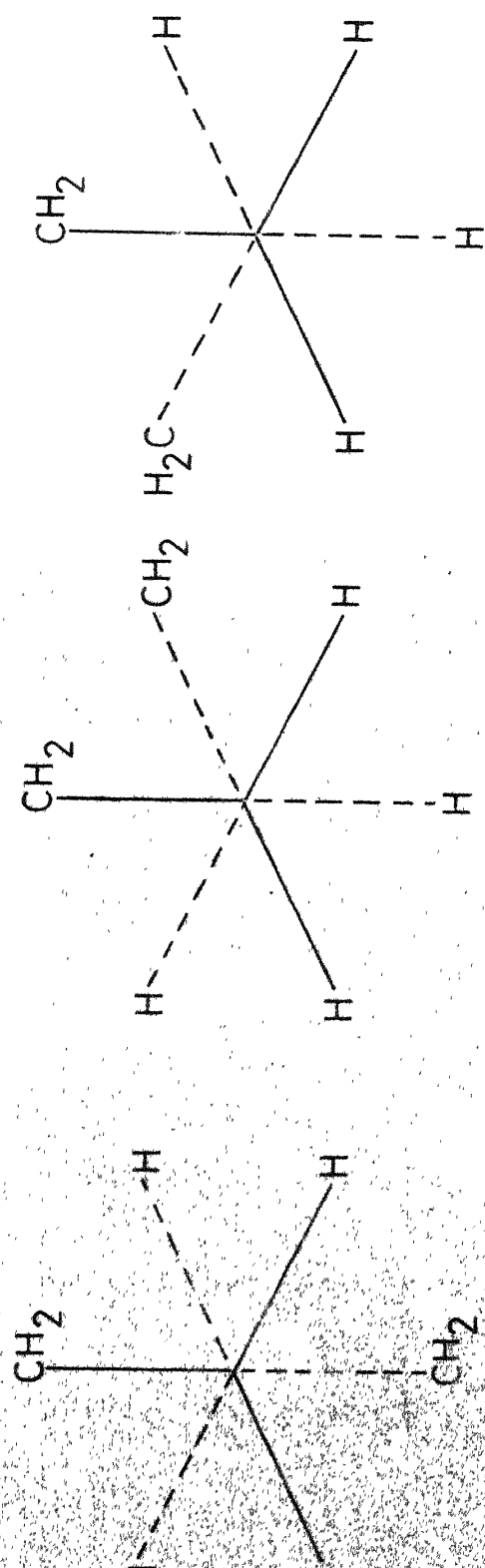


FIG. 3. ROTATIONAL ISOMERS OF POLYETHYLENE.

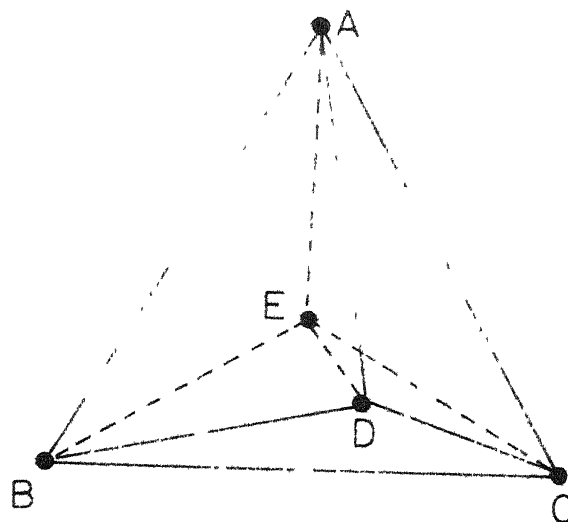


FIG.4a TETRAHEDRAL BONDS IN A DIAMOND LATTICE

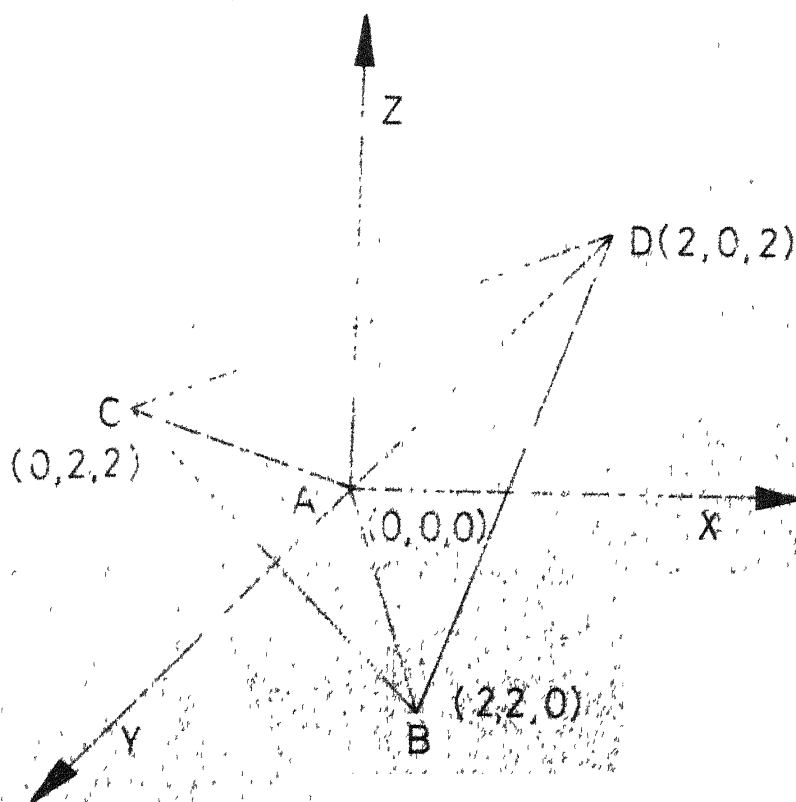


FIG.4b ORTHOGONAL SET OF AXES DESCRIBING THE
TETRAHEDRAL BONDS

The coordinates of the center (where the perpendiculars from any vertex to the opposite face meet) will be given by

$$\left(\frac{0+2+0+2}{4}, \frac{0+2+2+0}{4}, \frac{0+0+2+2}{4} \right) \text{ or } (1,1,1)$$

Hence the vector AE is given by $(1,1,1)$. Similarly other vectors are EB $(1,1,\bar{1})$, EC $(\bar{1},1,1)$ and ED $(1,\bar{1},1)$. In the case of an actual lattice, other vectors are also present but they are described with respect to the axes shown in Figure 4b. They will be given by $(\bar{1},\bar{1},1)$, $(\bar{1},1,\bar{1})$, $(1,\bar{1},\bar{1})$ and $(\bar{1},\bar{1},\bar{1})$. Thus, a set of eight vectors is obtained, which describe all the possible bonds. In solving the problem by the method of 'random-walk', these vectors also describe the direction of translation in going from one lattice point (atom) to the neighbouring one. This set can be symbolically written as $(1,1,1)$. From here, a property of the diamond lattice emerges, that each successive vector is obtained from the preceding one by changing the sign of one component and leaving the two others unchanged (a property which makes the Markoff chain method applicable to the system). The three possible orientations of a link have probabilities a or b according to whether it is placed in the trans or in one of the two gauche positions with respect to the two preceding links.

The probabilities a and b are determined by the relations

$$a + 2b = 1 \quad (2-48)$$

$$\frac{a}{b} = \exp\left(\frac{\varepsilon}{kT}\right) \quad (2-49)$$

where $\varepsilon = E_g - E_{tr}$ is the energy difference between a gauche and a trans sequence of three links.

Earlier Tobolsky⁶ calculated the expected square of the length of a hydrocarbon type chain by considering the random walk on a diamond lattice. He considered the probability for two successive changes in sign to occur at the same coordinate [i.e., $(X^{i+2}, Y^{i+2}, Z^{i+2})$ is identical to (X^i, Y^i, Z^i)] to be r and the probability for the second change of sign to occur at one of the other two places with probability $(1-r)/2$. These three situations correspond to the trans and the two gauche configurations.

Now substitute

$$(X^{(0)}, Y^{(0)}, Z^{(0)}) = (1, 1, 1) \quad (2-50)$$

and
$$U_i = X^{(i)} + Y^{(i)} + Z^{(i)} \quad (2-51)$$

Then from equation (2-14)

$$L_i = E(U_i) \quad (2-52)$$

The variable U_i can assume the four values $\pm 3, \pm 1$. Tobolsky⁶ considered the sequence of pairs $(U_0, U_1), (U_1, U_2),$

$(U_2, U_3) \dots (U_i, U_{i+1}) \dots (U_{n-1}, U_n)$, where each pair corresponds to a state with possible values $(3, 1)$, $(1, 3)$, $(1, -1)$, $(-1, 1)$, $(-1, -3)$ and $(-3, -1)$. The transition probability matrix can be given as

$$P = \begin{array}{c} \begin{array}{cc} & \begin{array}{cccccc} 1 & 1\ 3 & 1\ -1 & -1\ 1 & -1\ -3 & -3\ -1 \end{array} \\ \begin{array}{c} 3\ 1 \\ 1\ 3 \\ 1\ -3 \\ -1\ 1 \\ -1\ -3 \\ -3\ -1 \end{array} & \left[\begin{array}{cccccc} 0 & r & 1-r & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{1+r}{2} & \frac{1-r}{2} & 0 \\ 0 & \frac{1-r}{2} & \frac{1+r}{2} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1-r & r & 0 \end{array} \right] \end{array} \quad (2-53)$$

The expected square of the end-to-end distance $\langle R_n^2 \rangle$ for large values of n is obtained as follows,

$$\langle R_n^2 \rangle = (2+6r) n l_0^2 / 3(1-r) \quad (2-54)$$

In the present work a further modification of the Tobolsky's model is considered. A sequence of three consecutive links is taken. If the last one is parallel to the first, i.e., when the sign of the same coordinate has changed, it is assumed to occur with a probability r . This is the probability of the orientation being destroyed. Let the other two probabilities, i.e., of preserving the orientation (in the direction indicated by the arrow in Figure 2) and for reversing the orientation be designated as p and q

respectively. In other words, if two consecutive changes of sign involve the coordinates X and Y, then the next change occurs at the coordinate Y again with probability r, at the coordinate X with probability p and with probability q at the remaining coordinate.

Now the transition probability matrix is given below

$$\begin{array}{c}
 \begin{array}{cc}
 & \begin{array}{cc} 3 & 1 \end{array} \\
 \begin{array}{cc} 3 & 1 \end{array} & \begin{bmatrix} 0 & r & 1-r & 0 & 0 & 0 \end{bmatrix} \\
 \begin{array}{cc} 1 & 3 \end{array} & \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \\
 \begin{array}{cc} 1 & -1 \end{array} & \begin{bmatrix} 0 & 0 & 0 & p+r & q & 0 \end{bmatrix} \\
 \begin{array}{cc} -1 & 1 \end{array} & \begin{bmatrix} 0 & q & p+r & 0 & 0 & 0 \end{bmatrix} \\
 \begin{array}{cc} -1 & -3 \end{array} & \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \\
 \begin{array}{cc} -3 & -1 \end{array} & \begin{bmatrix} 0 & 0 & 0 & 1-r & r & 0 \end{bmatrix}
 \end{array}
 \end{array}
 \quad (2-55)$$

Obviously $p + q + r = 1$.

From equation (2-15) expected square of the end-to-end distance is given by

$$\langle R_n^2 \rangle = -3n + 2 \sum_{k=0}^{n-1} (n-k) L_k \quad (2-56)$$

where $L_k = E(X_o X_k + Y_o Y_k + Z_o Z_k)$

The chain can start in any one of the six states.

The weights assigned to the various states are

$$\begin{aligned}
 \omega_1 &= 3 \\
 \omega_2 &= \omega_3 = 1 \\
 \omega_4 &= \omega_5 = -1 \\
 \omega_6 &= -3
 \end{aligned}$$

With these, in general

$$E(X(s) X(t) + Y(s) Y(t) + Z(s) Z(t)) = \sum_{j,k=1}^6 p_{ij}^{(s)} \omega_j p_{jk}^{(t-s)} \omega_k \quad \dots(2-57)$$

where $p_{ij}^{(s)}$ is the s^{th} step transition probability from the state i to j . The matrix P has three eigenvectors of the symmetric pattern (X,Y,Z,Z,Y,X) , which will not contribute to L_k and three eigenvectors of the antisymmetric form $(X,Y,Z,-Z,-Y,-X)$ which would contribute to L_k . The eigenvalues corresponding to the antisymmetric eigenvectors are -1 , λ_1 and λ_2 , where λ_1 and λ_2 are roots of

$$\begin{aligned}
 \lambda_1 + \lambda_2 &= q \\
 \lambda_1 \lambda_2 &= q-r
 \end{aligned}$$

The $p_{ij}^{(k)}$ elements which contribute to L_k are given below

$$p_{11}^{(k)} = -p_{16}^{(k)} = -p_{61}^{(k)} = p_{66}^{(k)} = (-1)^k C_1 + \lambda_1^k C_2 + \lambda_2^k C_3 \quad (2-58a)$$

$$p_{12}^k = -p_{15}^k = -p_{62}^k = p_{65}^k = (-1)^{k+1} C_1 + \lambda_1^{k+1} C_2 + \lambda_2^{k+1} C_3 \quad (2-58b)$$

$$\begin{aligned}
 p_{13}^k = -p_{14}^k = -p_{63}^k = p_{64}^k &= (-1)^{k+1} \frac{1-r}{q} C_1 + \lambda_1^k (1-\lambda_1) C_2 \\
 &+ \lambda_2^k (1-\lambda_2) C_3 \quad \dots(2-58c)
 \end{aligned}$$

$$p_{21}^k = -p_{26}^k = -p_{51}^k = p_{51}^k = p_{56}^k = (-1)^{k+1} c_1 + \lambda_1^{k-1} c_2 + \lambda_2^{k-1} c_3 \quad \dots (2-58d)$$

$$p_{22}^k = p_{11}^k = -p_{25}^k = -p_{52}^k = p_{55}^k \quad (2-58e)$$

$$p_{23}^k = -p_{24}^k = -p_{53}^k = p_{54}^k = (-1)^k \frac{1-r}{q} c_1 + \lambda_1^{k-1} (1 - \lambda_1) c_2 + \lambda_2^{k-1} (1 - \lambda_2) c_3 \quad (2-58f)$$

$$p_{31}^k = -p_{36}^k = -p_{41}^k = p_{46}^k = (-1)^{k+1} c_1 + \frac{q(1 - \lambda_1)}{r-1} \lambda_1^{k-1} c_2 + \frac{q(1 - \lambda_2)}{r-1} \lambda_2^{k-1} c_3 \quad (2-58g)$$

$$p_{32}^k = -p_{13}^k = -p_{35}^k = -p_{42}^k = p_{45}^k \quad (2-58h)$$

$$p_{33}^k = -p_{34}^k = -p_{43}^k = p_{44}^k = (-1)^k \frac{1-r}{q} c_1 + \frac{q}{r-1} (1 - \lambda_1)^2 \lambda_1^{k-1} c_2 + \frac{q}{r-1} (1 - \lambda_2)^2 \lambda_2^{k-1} c_3 \quad \dots (2-58i)$$

where

$$c_1 = \frac{q}{2(2q+1-r)}, \quad c_2 = \frac{\lambda_1(1 - \lambda_2^2)}{2(\lambda_1 - \lambda_2)(2q+1-r)}, \quad c_3 = \frac{-\lambda_2(1 - \lambda_1^2)}{2(\lambda_1 - \lambda_2)(2q+1-r)}$$

Now

$$\sum_{k=1}^6 p_{jk}^{(n)} \omega_k = 3(p_{j1}^n - p_{j6}^n) + (p_{j2}^n - p_{j4}^n) + (p_{j3}^n - p_{j5}^n) = L_{jn} \quad (2-59)$$

The different values of j correspond to the chain starting in different initial states, and, thus, different values of L_k are obtained. As mentioned earlier, in order to obtain an 'ensemble' average the calculated $\langle R_n^2 \rangle$ is

weighted by the stationary state probabilities of the corresponding initial starting state.

For the six steady states, probabilities are given below

$$\frac{q}{2(2q+1-r)}, \frac{q}{2(2q+1-r)}, \frac{1-r}{2(2q+1-r)}, \frac{1-r}{2(2q+1-r)}, \frac{q}{2(2q+1-r)}, \frac{q}{2(2q+1-r)}$$

Substituting these values, we get,

$$L_k = \frac{q}{2q+1-r} L_{1k} + L_{2k} + \frac{1-r}{q} L_{3k} \quad (2-60)$$

On substituting various values following expression for L_k is obtained

$$L_k = \frac{q}{2q+1-r} \left[\frac{2C_1 (-1)^k}{q^2} (2q+1-r)^2 + 32C_2 \lambda_1^k + 32C_3 \lambda_2^k \right] \quad (2-61)$$

Now,

$$\sum_{k=0}^{n-1} (n-k) \lambda^k = \frac{n}{1-\lambda} + \frac{\lambda^{n+1}}{(1-\lambda)^2} - \frac{\lambda}{(1-\lambda)^2} \quad (2-62)$$

$$\sum_{k=0}^{n-1} (n-k) (-1)^k = A = \frac{n}{2} + \frac{(-1)^{n+1} + 1}{4} \quad (2-63)$$

Substituting equations (2-61 - 2-63) in equation (2-56) and considering large values of n , the value of the expected square of the end-to-end distance for an oriented hydrocarbon-type molecule is reduced to a simple expression

$$\langle R_n^2 \rangle = \left[-3n+2A \frac{2q(-1+r)^2}{2q+1-r} + \frac{128q}{4(2q+1-r)^2} \frac{n}{1-r} \{1+(q-r)(1-q)\} \right] \frac{1}{3} l_0^2 \quad \dots (2-64)$$

It should be possible to test the validity of this equation from measurements on light scattering, viscosity, etc., for hydrocarbons of various chain lengths. This would also permit an estimate of the various transition probability parameters and from measurements of $\langle R_n^2 \rangle$ on chains of different molecular weights, the self-consistency of these parameters could be checked.

The result for the special case of Tobolsky⁶ is obtained by substituting $q = \frac{1-r}{2}$, i.e., $p = q$. In this case, the expression for $\langle R_n^2 \rangle$ (equation 2-64) reduces to

$$\langle R_n^2 \rangle = \frac{2n}{1-r} \frac{1}{3} (1 + 3r) l_0^2 \quad (2-65)$$

$r = 1/3$ implies that there will be no energy difference between the trans and the two gauche configurations. Substituting $r = 1/3$ in equation (2-65), we get

$$\langle R_n^2 \rangle = 2n l_0^2 \quad (2-66)$$

and $r = 0$ implies that the trans configurations are nearly excluded. Substituting $r = 0$

$$\langle R_n^2 \rangle = \frac{2}{3} n l_0^2 \quad (2-67)$$

These results are well known in the theory of random walk.

In this problem, the transition probability matrix of the Markoff chain relates the orientation of the vector R_i to R_{i-1} and R_{i-2} . Correlations in the more distant links are disregarded. As a result of this limited memory of the links, it is not possible to prevent the occurrence of conformations containing loops or of conformations that are ruled out because of steric hindrance. This influence of excluded volume effects the average square length of alkane-type chains and this has been studied by Hijmans and Holleman⁷ by excluding cyclohexane type loops and configurations involving pentane type steric hindrances. Such calculations approximate the physical situation much better.

REFERENCES

1. W. Feller, An Introduction to Probability Theory, 2nd edn. (New York: John Wiley), pp 338-49, 380-5.
2. E.W. Montroll, J. Chem. Phys., 18, 734 (1950).
3. A.V. Tobolsky and V.D. Gupta, J. Chem. Phys., 36, 1999 (1962).
4. J.W. Wilchensky, J. Poly. Sc., A-2, 6, 281 (1968).
5. M.V. Volkenstein, Configurational Statistics of Polymeric Chains, (New York: John Wiley), pp 208.
6. A.V. Tobolsky, J. Chem. Phys., 31, 387 (1959).
7. J. Hijmans and T. Holleman, J. Chem. Phys. 36, 47 (1962).

CHAPTER - III

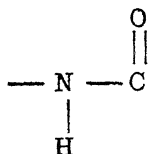
PHASE TRANSITIONS IN POLYMERIC SYSTEMS3.1 INTRODUCTION

A system is said to undergo phase transition when there is a sudden change in its properties with respect to some thermodynamic parameters such as temperature, concentration, etc. A transition is said to be of the n th order when the n th derivative of free energy with respect to any of its natural thermodynamic variables has a discontinuity. For example, melting of crystal, helix-random coil transitions, etc. are termed as first order transition, whereas superconducting transitions in zero field and λ transitions like order-disorder transformation in β brass // and transition in ortho hydrogen are termed as second-order transitions. In the present work, the problem of phase transition in some finite macromolecular systems is studied. In case of helical polypeptides, this problem has been studied by Zimm and Bragg¹, Lifson and Roig², Gibbs and Di Marzio³ and others⁴⁻⁶. The theoretical treatment is based on one-dimensional models.

Actually, a polymer is a three-dimensional system but it is observed that in the neighbourhood of transition a one-dimensional model gives a good description of its properties. It has been shown^{7,8} that a one-dimensional

system does not exhibit phase transition, if it is assumed that the interaction has a finite range and is non-singular. If these two restrictions are relaxed, then the system does show a transition from one to the other state. Based on these considerations, which is essentially a modification of the Ising model, Zimm and Bragg¹ besides several others²⁻⁶ have given a theory for the helix-coil transition in simple polypeptides.

The polypeptide chain consists of amide groups



connected by intermediary carbon atoms.

In the α -helix, the hydrogen atom of each amide group forms a hydrogen bond with the oxygen atom of the third preceding amide group, i.e., each segment is bonded to the fourth subsequent segment as shown in Figure 5. Here an amide group plus one adjacent carbon is referred to as a segment of the chain.

Formation of a helical region is a cooperative phenomenon, i.e., once first segment is bonded to the fourth, it is relatively easy for the second segment to bind to the fifth and third to the sixth and so on. It is difficult for the first segment to bind due to a large loss in entropy. Once formed, however, this, in turn,

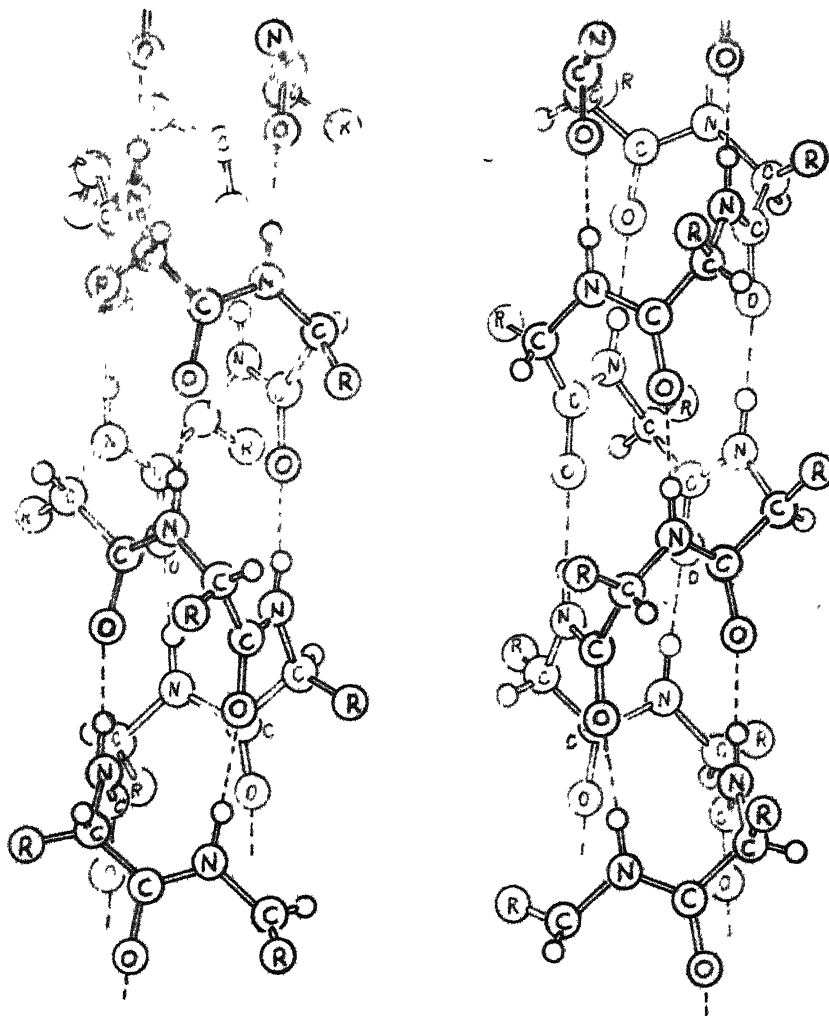


FIG.5. THE PAULING COREY ALPHA HELIX BOTH A RIGHT-HANDED AND A LEFT-HANDED HELIX ARE SHOWN

acts as a nucleus to which further turns can be added by hydrogen bonding. This difficulty in binding is expressed by a parameter called the nucleation parameter σ . A change of a few degrees in temperature or a few per cent in solvent composition can convert the randomly coiled form to the α -helix. Actually, this change in temperature and solvent composition brings a decrease in entropy which is essential for the formation of hydrogen bond.

Zimm and Bragg¹ have done the problem of transition between the helical and randomly coiled forms of a polypeptide chain. Two principal parameters introduced are (i) a statistical one that is essentially an equilibrium constant for the bonding of segments to a portion of the chain which is already in helical form, and (ii) a nucleation parameter. The partition function is calculated from the Ising matrix as the n th power of its maximum root. Helicity as a function of temperature is calculated for polybenzylglutamate and is in good agreement with experimental data. Poland and Sheraga⁹ in a recent publication have given a comparison of theories of helix-coil transition in polypeptides. Lifson and Roig² have used a sequence generating function whereas Peller⁶ has used a combinatorial approach. In the former, a cubic secular equation is obtained, the maximum root of which is approximated by a quadratic equation. If the use of triplets as units is replaced by

the use of amino acid residues and the positive energy of formation of a hydrogen bond is assigned to single helical states, then the Peller's result is identical to the quadratic approximation.

3.2 CELL MODEL FOR DIFFUSE PHASE TRANSITION

The cell model has been applied to explain λ point anomaly found in ammonium hexafluoro-silicate, NH_4Cl , KH_2PO_4 , KH_2AsO_4 , $\text{Ag}_2\text{H}_3\text{IO}_6$ and CH_4 . It has also been applied to explain thermally induced phase transition in a number of single strand and double strand helices^{10,11}. In the present work, the cell model has been used to study melting phenomenon in finite systems. This model can be briefly explained as follows.

Consider a lattice having two phases, A and B, dispersed in each other. Assume that each region of phase A or of phase B is wholly enclosed by a boundary and that the same coordination number Z is valid for their lattices. Suppose that the pair partition functions for aa, ab and bb pairs are f_{aa} , f_{ab} and f_{bb} respectively.

Consider a cell model for the total lattice of n molecules. For a molecule in the interior of one of the phase A regions, the contribution to the total partition function is $f_{aa}^{Z/2}$; for a molecule on the boundary of a phase A region, the contribution to the lattice partition function is (for simple boundaries) $f_{aa}^{Z/4} f_{ab}^{Z/4}$; for a

molecule in the interior of one of the phase B regions
 the contribution is $f_{bb}^{z/2}$ and for a molecule on the
 boundary of a phase B region, the contribution is
 $f_{bb}^{z/4} f_{ab}^{z/4}$.

The partition function for the lattice as a whole
 is solved by the Ising matrix method. The matrix is

$$P = \begin{array}{cc} & \begin{array}{cc} a & b \end{array} \\ \begin{array}{c} a \\ b \end{array} & \left[\begin{array}{cc} f_{aa}^{z/2} & f_{aa}^{z/4} f_{ab}^{z/4} \\ f_{bb}^{z/4} f_{ab}^{z/4} & f_{bb}^{z/2} \end{array} \right] \end{array} \quad (3-1)$$

The partition function Q for the entire lattice is

$$Q = \lambda_1^n + \lambda_2^n \quad (3-2)$$

where λ_1 and λ_2 are the roots of matrix P .

3.3 MELTING OF N-PARAFFIN HYDROCARBONS

The present modification consists of expressing
 the Ising matrix in terms of segment pair partition
 functions which are either in the amorphous region (denoted
 by r) or in the crystalline region (denoted by h). The
 boundary between the crystalline and amorphous states,
 i.e., the first h segment in a sequence of h states is
 denoted by a k state. f_r , f_h and f_k are the corresponding
 segment partition functions of the three states. Taking

into account the nearest-neighbour interaction, the basic matrix for the problem is

$$P = \begin{matrix} & \begin{matrix} r & k & h \end{matrix} \\ \begin{matrix} r \\ k \\ h \end{matrix} & \begin{bmatrix} f_r^{\frac{1}{2}} & f_r^{\frac{1}{2}} & 0 \\ f_r^{\frac{1}{2}} & f_k^{\frac{1}{2}} & f_k^{\frac{1}{2}} f_h^{\frac{1}{2}} \\ f_h^{\frac{1}{2}} & f_r^{\frac{1}{2}} & f_h^{\frac{1}{2}} f_k^{\frac{1}{2}} \end{bmatrix} \end{matrix} \quad (3-3)$$

The partition function for the entire system is obtained and the matrix method is used to obtain fractional crystallinity and average sequence length in the amorphous and crystalline regions. The results obtained are valid for an arbitrary and finite value of N , where N is the number of segments in the chain. This enables one to study the melting phenomenon in normal paraffin hydrocarbons.

The eigenvalues of P are given by

$$\begin{aligned} \lambda_1 &= \left[\frac{1}{2} (f_r + f_h) + \sqrt{(f_r - f_h)^2 + 4f_r f_k} \right] \\ \lambda_2 &= \frac{1}{2} \left[(f_r + f_h) - \sqrt{(f_r - f_h)^2 + 4f_r f_k} \right] \\ \lambda_3 &= 0 \end{aligned} \quad (3-4)$$

The matrix T which diagonalises P is given below

$$T = \begin{bmatrix} 1 & 1 & 1 \\ \frac{\lambda_1 - f_r}{f_r^{\frac{1}{2}} f_k^{\frac{1}{2}}} & \frac{\lambda_2 - f_r}{f_r^{\frac{1}{2}} f_k^{\frac{1}{2}}} & -f_r^{\frac{1}{2}} f_k^{-\frac{1}{2}} \\ \frac{f_h^{\frac{1}{2}} f_r^{\frac{1}{2}}}{\lambda_1 - f_h} & \frac{f_h^{\frac{1}{2}} f_r^{\frac{1}{2}}}{\lambda_2 - f_h} & -f_r^{\frac{1}{2}} f_h^{-\frac{1}{2}} \end{bmatrix} \quad (3-5)$$

Similarly T^{-1} can be written as

$$T^{-1} = \begin{bmatrix} C_1 & \frac{C_1 f_r^{\frac{1}{2}} f_k^{\frac{1}{2}}}{\lambda_1} & \frac{C_1 f_r^{\frac{1}{2}} f_k f_h^{\frac{1}{2}}}{\lambda_1 (\lambda_1 - f_h)} \\ C_2 & \frac{C_2 f_r^{\frac{1}{2}} f_k^{\frac{1}{2}}}{\lambda_2} & \frac{C_2 f_r^{\frac{1}{2}} f_k f_h^{\frac{1}{2}}}{\lambda_2 (\lambda_2 - f_h)} \\ 0 & C_3 & -C_3 f_k^{\frac{1}{2}} f_h^{-\frac{1}{2}} \end{bmatrix} \quad (3-6)$$

$$\text{where } C_1 = \frac{\lambda_1 - f_h}{\lambda_1 - \lambda_2}, \quad C_2 = \frac{\lambda_2 - f_h}{\lambda_2 - \lambda_1},$$

$$\text{and } C_3 = \frac{1}{f_r^{\frac{1}{2}} f_k^{\frac{1}{2}} f_h^{-1} - f_r^{\frac{1}{2}} f_k^{-\frac{1}{2}}}$$

Let the first segment be assumed in the amorphous phase (gauche configuration). Its contribution to the partition function is given by

$$U = (f_r^{\frac{1}{2}}, 0, 0) \quad (3-7)$$

The way the matrix P is constructed, the configurations ending with r , k or h have to be multiplied with $f_r^{\frac{1}{2}}$, $f_k^{\frac{1}{2}}$, $f_h^{\frac{1}{2}}$ respectively before their contribution is summed to

give the partition function. For this purpose, a column matrix U^\dagger is defined.

$$U^\dagger = \begin{bmatrix} f_r^{\frac{1}{2}} \\ f_k^{\frac{1}{2}} \\ f_h^{\frac{1}{2}} \end{bmatrix} \quad (3-8)$$

Now the partition function is given by

$$Z = U P^{N-1} U^\dagger = U T T^{-1} P^{N-1} T T^{-1} U^\dagger \quad (3-9)$$

From equations (3-3) to (3-8)

$$U T = (f_r^{\frac{1}{2}}, f_r^{\frac{1}{2}}, f_r^{\frac{1}{2}})$$

$$T^{-1} U^\dagger = \begin{bmatrix} c_1 f_r^{-\frac{1}{2}} & \lambda_1 \\ c_2 f_r^{-\frac{1}{2}} & \lambda_2 \\ 0 \end{bmatrix}$$

and

$$T^{-1} P T^{N-1} = \begin{bmatrix} \lambda_1^{N-1} & 0 & 0 \\ 0 & \lambda_2^{N-1} & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

Therefore, the expression (3-9) for partition function becomes

$$\begin{aligned}
 Z &= UT [T^{-1} PT]^{N-1} T^{-1} U^\dagger \\
 &= \begin{pmatrix} f_r^{\frac{1}{2}} & f_r^{\frac{1}{2}} & f_r^{\frac{1}{2}} \end{pmatrix} \begin{bmatrix} \lambda_1^{N-1} & 0 & 0 \\ 0 & \lambda_2^{N-1} & 0 \\ 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} C_1 & \lambda_1 f_r^{-\frac{1}{2}} \\ C_2 & \lambda_2 f_r^{-\frac{1}{2}} \\ 0 & 0 \end{bmatrix} \quad (3-10)
 \end{aligned}$$

or

$$\begin{aligned}
 Z &= C_1 \lambda_1^N + C_2 \lambda_2^N \\
 &= Z_1 + Z_2 \quad (3-11)
 \end{aligned}$$

Let the number of r segments, k segments and h segments (exclusive of k segments) be denoted by n_r , n_k and n_h^* . These values are given as follows,

$$\begin{aligned}
 \frac{n_r}{N} &= \frac{1}{N} \frac{\partial \ln Z}{\partial \ln f_r} \\
 &= \frac{f_r}{Z} \left[\frac{Z_1}{\lambda_1} \frac{\partial \lambda_1}{\partial f_r} + \frac{Z_2}{\lambda_2} \frac{\partial \lambda_2}{\partial f_r} \right] \\
 &\quad + \frac{f_r}{NZ} \left[\frac{Z_1}{\partial f_r} \frac{\partial \ln C_1}{\partial f_r} + \frac{Z_2}{\partial f_r} \frac{\partial \ln C_2}{\partial f_r} \right] \quad (3-12)
 \end{aligned}$$

$$\frac{n_k}{N} = \frac{f_k}{Z} \left[\frac{Z_1}{\lambda_1} \frac{\partial \lambda_1}{\partial f_k} + \frac{Z_2}{\lambda_2} \frac{\partial \lambda_2}{\partial f_k} \right] + \frac{f_k}{NZ} \left[\frac{Z_1}{\partial f_k} \frac{\partial \ln C_1}{\partial f_k} + \frac{Z_2}{\partial f_k} \frac{\partial \ln C_2}{\partial f_k} \right] \quad (3-13)$$

and

$$\frac{n_h^*}{N} = \frac{f_h}{Z} \left[\frac{Z_1}{\lambda_1} \frac{\partial \lambda_1}{\partial f_h} + \frac{Z_2}{\lambda_2} \frac{\partial \lambda_2}{\partial f_h} \right] + \frac{f_h}{NZ} \left[\frac{Z_1}{\partial f_h} \frac{\partial \ln C_1}{\partial f_h} + \frac{Z_2}{\partial f_h} \frac{\partial \ln C_2}{\partial f_h} \right] \quad (3-14)$$

These expressions finally reduce to the following, if we substitute

$$\frac{f_h}{f_r} = Y \quad (3-15)$$

$$\frac{f_k}{f_r} = \sigma \quad (3-16)$$

$$A = Z_1/Z \quad (3-17)$$

and

$$(\lambda_1 - \lambda_2)/f_r = P \quad (3-18)$$

$$\frac{n_r}{N} = \frac{1}{2} + \frac{1-Y}{2P} (2A-1) + \frac{1+Y}{2P^2N} [(2A-1)P - 1 + Y] \quad (3-19)$$

$$\frac{n_k}{N} = \frac{-\sigma(1+Y+P)}{2P(Y-\sigma)} + \frac{A\sigma(1+Y)}{(Y-\sigma)P} - \frac{(1-Y)}{2NP^2} [(2A-1)P - 1 + Y] \quad (3-20)$$

$$\frac{n_h^*}{N} = \frac{Y}{P} \left[\frac{1-Y+P}{1+Y-P} \right] - \frac{AY(1-Y+2\sigma)}{P(Y-\sigma)} - \frac{Y}{NP^2} [(2A-1)P - 1 + Y] \quad \dots(3-21)$$

It can be immediately checked that

$$\frac{n_r}{N} + \frac{n_k}{N} + \frac{n_h^*}{N} = 1 \quad (3-22)$$

Inasmuch as we use segment partition functions, these quantities can be interpreted in the following manner,

$$f_r = \epsilon_r \quad (3-23)$$

$$f_h = \epsilon_h \exp \left(\frac{\Delta H_f}{RT} \right) \quad (3-24)$$

$$f_k = \epsilon \quad (3-25)$$

where g_r is the statistical weight of an r segment, g_h is the statistical weight of an h segment and ΔH_f is the heat of fusion from the crystalline to amorphous state.

The partition function f_k of the k segments which represent the boundary between amorphous and crystalline regions is taken to be temperature independent and very small so as to represent the difficulty encountered in entering such a boundary region. In equations (3-23 - 3-25), g_h , g_r and ϵ are assumed to be constants, and ΔH_f is the heat of fusion per mole of segments. For large N at the fusion point, f_h is equal to f_r . The temperature of fusion and the entropy of fusion are, therefore, given by

$$T_f = \Delta H_f / R \ln(g_r/g_h) = \Delta H_f / \Delta S_f \quad (3-26)$$

where $\Delta S_f = R \ln(g_r/g_h)$

$$\text{Hence } Y = \frac{f_h}{f_r} = \frac{g_h}{g_r} \exp(\Delta H_f / RT) \quad (3-27)$$

$$= \exp [(\Delta H_f - \Delta S_f T) / RT]$$

$$= \exp \left[\frac{\Delta H_f}{T T_f R} (T_f - T) \right] = e^x \quad (3-28)$$

where $x = \frac{\Delta H_f}{T T_f R} (T_f - T)$

and $\sigma = \frac{f_k}{f_r} = \frac{\epsilon}{g_r}$

The number of amorphous sequences \bar{r} and that of helical sequences \bar{h} are given by

$$\bar{r} = n_r/n_k \quad (3-29)$$

$$\bar{h} = \frac{n_h^* + n_k}{n_k} \quad (3-30)$$

Let Q be the fractional crystallinity, then

$$Q = 1 - \frac{n_r}{N} \quad (3-31)$$

or
$$\frac{n_r}{N} = (1-Q) \quad (3-32)$$

Now the density d of a macromolecule with large N can be written as

$$d = QC + (1 - Q) A \quad (3-33)$$

where C and A are partial densities of crystalline and amorphous parts.

Value of C can be obtained by taking the crystallinity and density values at $N = 30$, as the experimental¹² density curve is available for this value of chain length

Now at

$$T = 273^\circ\text{K}$$

and $Q = 0.865$

$$d = 0.952.$$

This gives $C = 0.979.$

At sufficiently high temperatures,

$$Q = 0$$

therefore, $A = d_o$

where d_o is the density of the amorphous part and its value as given by Flory, Orwoll and Vrij¹³ is 0.779.

Substituting the values of C and A in equation (3-33), we get

$$d = 0.2Q + 0.779 \quad (3-34)$$

Normal paraffins for odd $N \geq 9$ and for even $N \geq 44$ exist in the orthorhombic crystalline form. Transition from the orthorhombic to the hexagonal form precedes melting for odd N in the range $11 \leq N \leq 43$ and for even N , $34 \leq N \leq 42$. Flory and Vrij¹⁴ have reported the melting points and enthalpies of fusion for $N = 15, 19, 25, 29, 30$ and 43. Their data is given in Table 1.

TABLE 1

Chain length N	Enthalpies of fusion ΔH	Melting point °K
15	700	280.5
19	750	302.5
25	800	324.5
29	805	330.0
30	795	336.0
43	800	358.0

Use has been made of the above data in obtaining the melting curves Q versus T . The calculated data is given in Table 2.

TABLE 2

CRYSTALLINITY VS. TEMPERATURE FOR
VARIOUS CHAIN LENGTHS AND σ VALUES

Temperature °K	Crystallinity 2					
	N = 15			N = 19		
	$\sigma = 10^{-2}$	$\sigma = 2 \times 10^{-3}$	$\sigma = 10^{-4}$	$\sigma = 10^{-2}$	$\sigma = 6 \times 10^{-4}$	$\sigma = 10^{-4}$
250	0.747	0.717	0.348	0.814	0.812	0.769
260	0.719	0.669	0.241	0.795	0.783	0.694
270	0.687	0.611	0.163	0.773	0.742	0.587
280	0.652	0.546	0.110	0.748	0.686	0.457
290	0.613	0.477	0.075	0.720	0.612	0.330
300	0.572	0.409	0.052	0.688	0.524	0.226
310	0.529	0.346	0.037	0.652	0.430	0.151
320	0.487	0.290	0.027	0.612	0.341	0.100
330	0.445	0.242	0.020	0.570	0.263	0.068
340	0.405	0.202	0.016	0.527	0.201	0.047
350	0.369	0.170	0.012	0.483	0.153	0.033
360	0.335	0.143	0.009	0.441	0.118	0.024
370	0.304	0.122	0.008	0.400	0.091	0.018
380	0.277	0.105	0.006	0.362	0.072	0.014
390	0.253	0.091	-	0.328	0.057	0.010
400	0.231	0.079	-	0.297	0.047	0.008
410	0.212	0.070	-	0.269	0.038	0.007
420	0.196	0.062	-	0.245	0.032	-
430	0.181	0.056	-	0.223	0.027	-
440	0.168	0.050	-	0.205	0.024	-
450	0.157	0.046	-	0.188	0.020	-
460	0.147	0.042	-	0.174	0.018	-
470	0.138	0.039	-	0.161	0.016	-

(contd.)

Table 2 (contd.)

Temperature °K	Crystallinity					
	Q					
	N = 25			N = 29		
	$\sigma = 10^{-2}$	$\sigma = 2 \times 10^{-4}$	$\sigma = 10^{-4}$	$\sigma = 10^{-3}$	$\sigma = 10^{-4}$	$\sigma = 10^{-5}$
250	0.865	0.872	0.871	0.890	0.890	0.890
260	0.851	0.858	0.857	0.879	0.879	0.877
270	0.835	0.841	0.838	0.866	0.866	0.859
280	0.816	0.818	0.8	0.851	0.850	0.824
290	0.795	0.783	0.758	0.834	0.827	0.750
300	0.771	0.728	0.678	0.813	0.791	0.612
310	0.743	0.646	0.561	0.786	0.730	0.421
320	0.711	0.537	0.423	0.750	0.632	0.244
330	0.675	0.413	0.292	0.702	0.499	0.127
340	0.635	0.296	0.191	0.638	0.355	0.065
350	0.592	0.204	0.122	0.559	0.232	0.034
360	0.547	0.138	0.078	0.468	0.145	0.018
370	0.500	0.093	0.051	0.376	0.090	0.011
380	0.454	0.064	0.034	0.292	0.057	0.006
390	0.410	0.045	0.024	0.223	0.037	-
400	0.369	0.033	0.017	0.170	0.025	-
410	0.331	0.025	0.013	0.130	0.017	-
420	0.298	0.019	0.009	0.101	0.013	-
430	0.268	0.015	-	0.079	0.009	-
440	0.242	0.012	-	0.064	-	-
450	0.220	0.010	-	0.052	-	-
460	0.200	0.008	-	0.044	-	-
470	0.183	0.007	-	0.037	-	-

(contd.)

Table 2 (contd.)

Temperature °K	Crystallinity					
	N = 30			N = 43		
	$\sigma = 10^{-3}$	$\sigma = 9 \times 10^{-5}$	$\sigma = 10^{-5}$	$\sigma = 10^{-3}$	$\sigma = 5 \times 10^{-5}$	$\sigma = 10^{-5}$
250	0.892	0.893	0.893	0.925	0.926	0.926
260	0.881	0.882	0.881	0.917	0.918	0.918
270	0.869	0.869	0.864	0.908	0.910	0.910
280	0.854	0.854	0.835	0.898	0.900	0.900
290	0.838	0.832	0.774	0.887	0.889	0.889
300	0.817	0.798	0.654	0.873	0.876	0.874
310	0.791	0.742	0.471	0.857	0.859	0.853
320	0.758	0.648	0.283	0.837	0.835	0.813
330	0.712	0.516	0.150	0.812	0.797	0.722
340	0.652	0.369	0.076	0.781	0.726	0.547
350	0.575	0.240	0.039	0.739	0.597	0.325
360	0.486	0.149	0.021	0.682	0.418	0.158
370	0.394	0.091	0.012	0.606	0.248	0.071
380	0.308	0.057	0.007	0.512	0.133	0.033
390	0.236	0.034	-	0.409	0.071	0.016
400	0.179	0.025	-	0.312	0.038	0.008
410	0.137	0.017	-	0.231	0.022	-
420	0.106	0.013	-	0.170	0.014	-
430	0.084	0.009	-	0.126	0.009	-
440	0.067	0.007	-	0.096	-	-
450	0.055	-	-	0.075	-	-
460	0.046	-	-	0.059	-	-
470	0.039	-	-	0.049	-	-

The nucleation parameter $\frac{f_k}{f_r}$ is adjusted to give correct melting point. Crystallinity versus temperature curves are shown in Figures 6a-6f. The dependence of transition curves on σ values is also shown and, as expected, it becomes sharper for small values.

Seyer, Peterson and Keays¹² have reported the variation of density with temperature. These results can be compared with the values of density obtained from equation (3-34). The experimental results and theoretical calculations for $N = 30$ are shown in Figure 7. The corresponding data is given below in Table 3.

TABLE 3

Temperature °K	Experimental Density gm. cm ⁻³	Calculated Density gm. cm ⁻³
275	0.951	0.951
300	0.940	0.939
325	0.929	0.899
350	0.780	0.830
375	0.773	0.795

Because of the equivalence of the crystal structures for polyethylene and N-paraffin hydrocarbons and the virtual identity of their unit cell dimensions, it is expected that the limiting melting point for N-paraffin hydrocarbon series

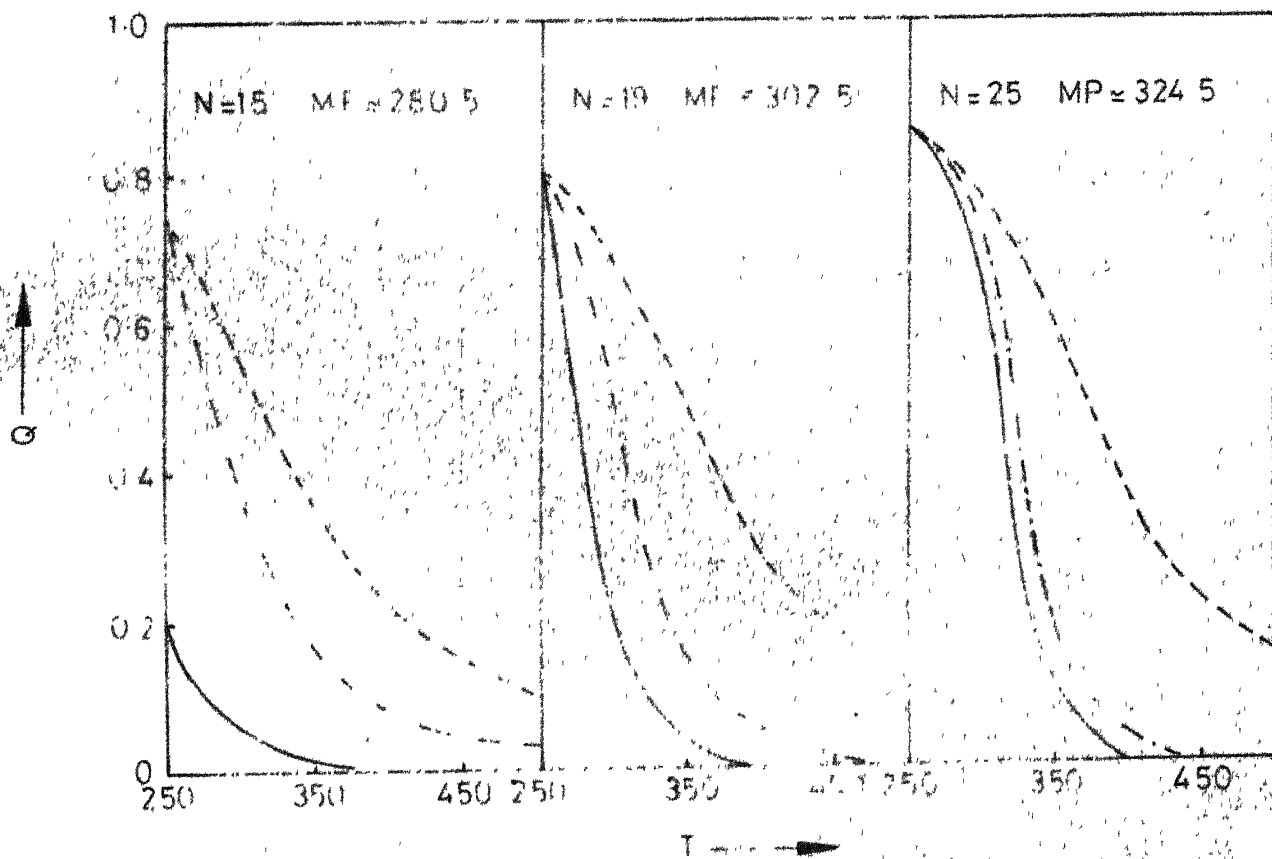


FIG. 6a.

FIG. 6b.

FIG. 6c.

CRYSTALLINITY AGAINST TEMPERATURE CURVES FOR DIFFERENT VALUES OF CHAIN LENGTH

— $\sigma = 10^{-2}$

- - - $\sigma = 10^{-4}$

- · - $\sigma = 2 \times 10^{-3}, 6 \times 10^{-4}, 2 \times 10^{-4}$ FOR FIGURES 6a, 6b AND 6c RESPECTIVELY

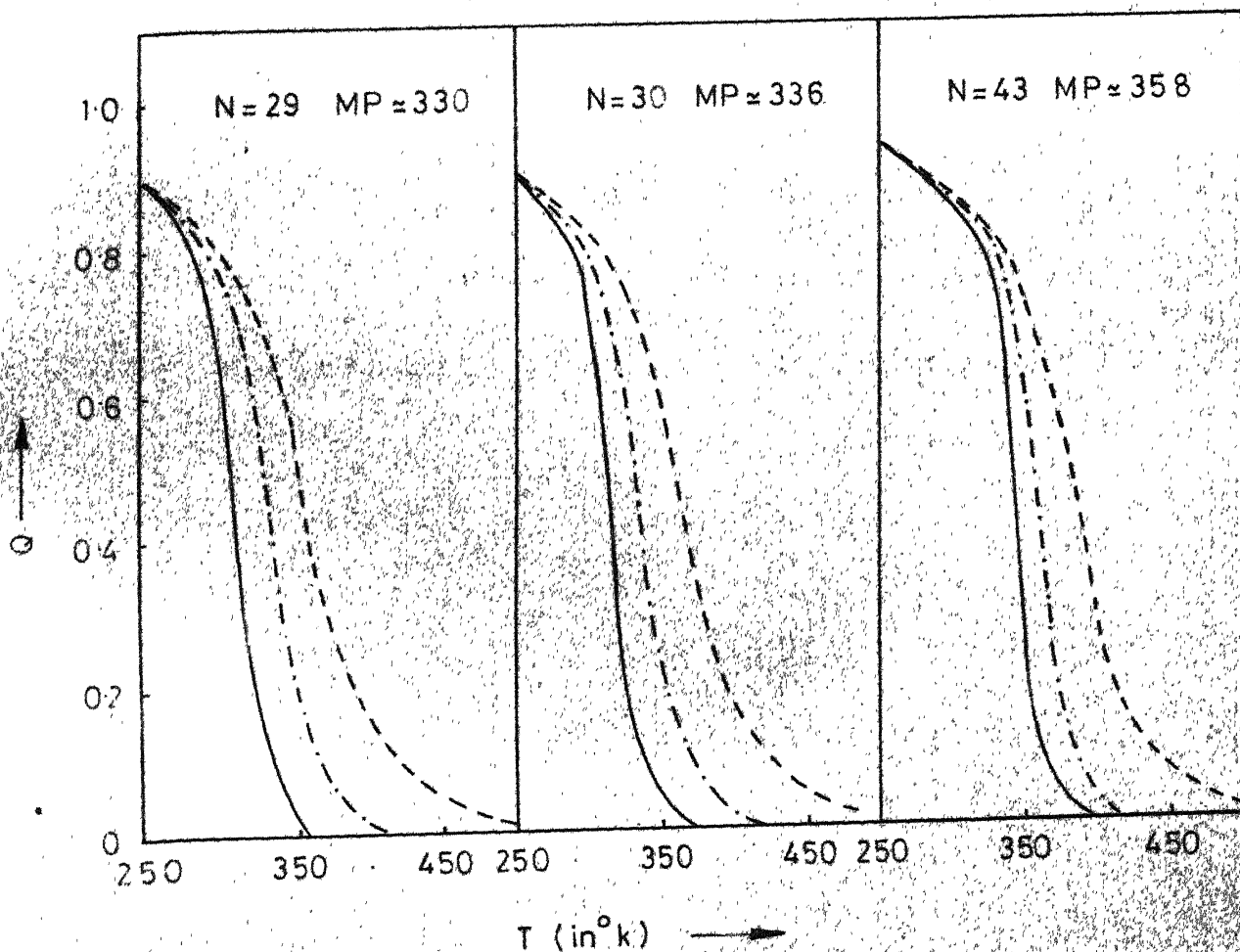


FIG. 6d.

FIG. 6e.

FIG. 6f.

CRYSTALLINITY AGAINST TEMPERATURE CURVES FOR DIFFERENT VALUES OF CHAIN LENGTH.

— $\sigma = 10^{-3}$

- - - $\sigma = 10^{-5}$

· · · $\sigma = 10^{-4}, 9 \times 10^{-5}, 5 \times 10^{-5}$, FOR FIGURES 6d, 6e AND 6f RESPECTIVELY.

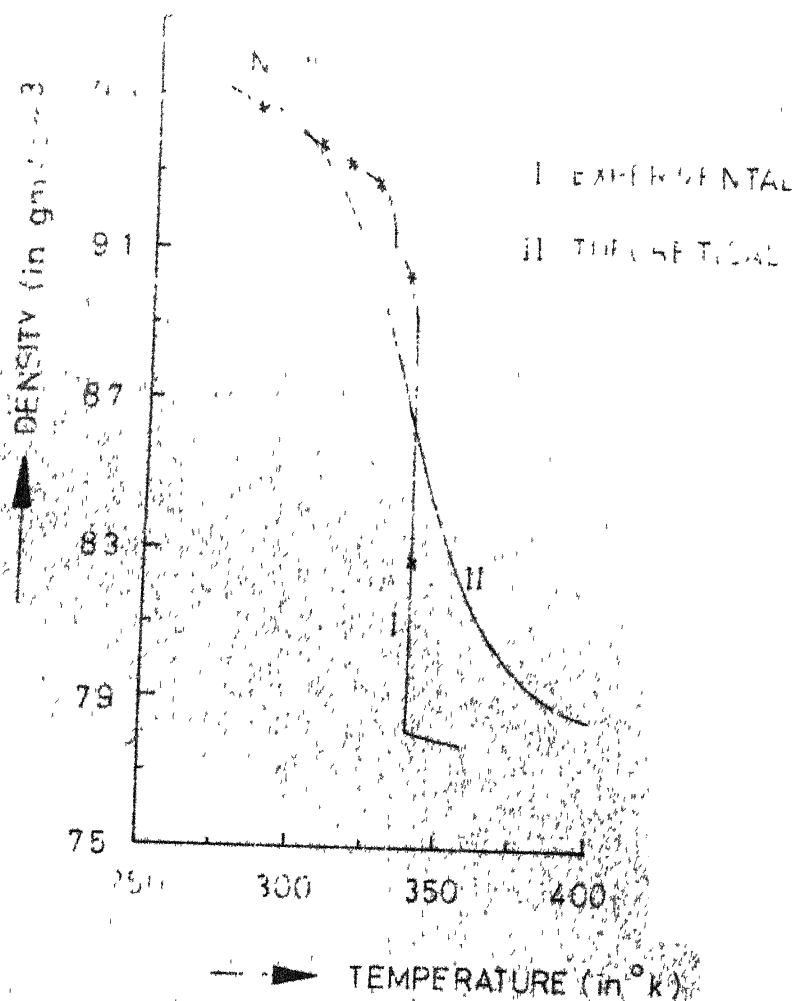


FIG. 7. DENSITY VERSUS TEMPERATURE CURVES FOR N_2

must be coincident with the melting point for linear polyethylene of infinite chain length. This is supported by the curve shown in Figure 8. The value of the nucleation parameter also asymptotically approaches the value 5×10^{-6} (Figure 9), which yields correct results for polyethylene. Table 4 gives the values of nucleation parameter for different chain lengths.

TABLE 4

Chain length N	Nucleation parameter $\sigma = \frac{f_k}{f_r}$
15	2×10^{-3}
19	6×10^{-4}
25	2×10^{-4}
29	1×10^{-4}
30	9×10^{-5}
43	5×10^{-5}

3.4 EFFECT OF PRESSURE ON TRANSITION IN POLYETHYLENE

The mechanical behaviour and morphological structure of a polymeric material are markedly changed when subjected to stress. For example, the elongation of a network polymer in the amorphous state increases its free energy and if the polymer is capable of crystallinity, its melting point will

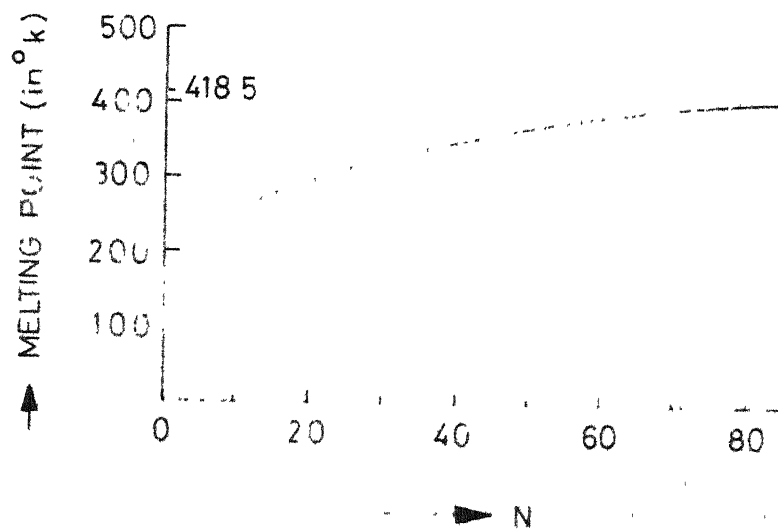


FIG. 8 MELTING POINT V. CHAIN LENGTH

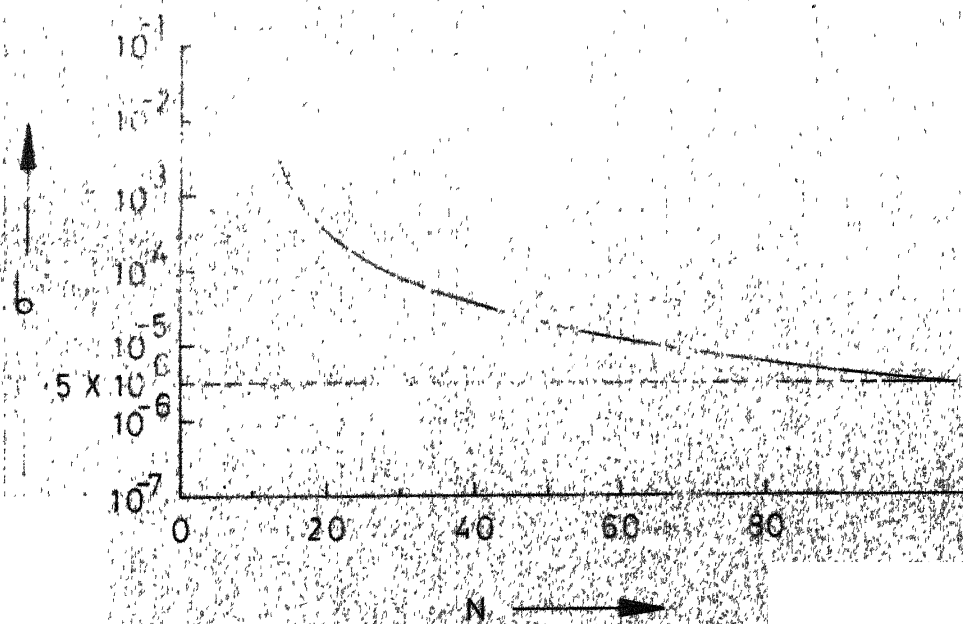


FIG. 9 VARIATION OF σ WITH CHAIN LENGTH

also be increased. Vulcanised rubber which does not crystallize at ordinary temperature becomes highly crystalline when sufficiently elongated, even at temperature above 100°C. Matsucka¹⁵ has argued that the overall specific volume below the melting point is not a unique function of pressure and temperature and hence may not be regarded as a thermodynamic quantity. However, a temperature-pressure relationship is very useful in estimating the true melting point as a function of pressure. The problem regarding the effect of pressure on melting point has also been studied by Krigbaum¹⁶. The melting point increases as the applied pressure is increased and can be represented by equating Gibb's free energy of fusion to zero. For segments within a sufficiently large crystalline domain,

$$\Delta G = \Delta U + P \Delta V_u - T \Delta S_u \quad (3-35)$$

where ΔG is the free energy, ΔU is the internal energy of fusion, P is the pressure, ΔV_u is the volume of fusion, T is the absolute temperature and ΔS_u is the entropy of fusion. The change in melting temperature due to the applied pressure is given by Clapeyron's equation

$$dT_m/dP = T_m \Delta V_u / \Delta H_u \quad (3-36)$$

where ΔV_u and ΔH_u are the change in volume and change

in enthalpy at the melting temperature T_m .

In the present work the formalism of the Ising model for a linear chain of spins in a magnetic field has been applied to study the effect of pressure on the transition curve for polyethylene. When a polymer segment is subjected to stress, the contribution of a segment to partition function in crystalline or amorphous region is also altered. In the absence of any pressure, the contribution of the segments in the disordered and ordered state are f_r and f_h respectively and for the first ordered state in a sequence of ordered states, this contribution is f_k . When pressure is applied, the contribution of a segment in the crystalline or helical state relative to an amorphous state may be written as ff_h where $f = e^{-\Delta E/RT}$, ΔE being the energy difference between the two states due to the pressure alone. The corresponding Ising matrix now becomes

$$W = \begin{matrix} & \begin{matrix} r & k & h \end{matrix} \\ \begin{matrix} r \\ k \\ h \end{matrix} & \begin{bmatrix} f_r & f_k & 0 \\ f_r & 0 & ff_h \\ f_r & 0 & ff_h \end{bmatrix} \end{matrix} \quad (3-37)$$

The partition function for the entire system is obtained by the same procedure as done in the previous problem.

The eigenvalues are given by the following relations

$$\lambda_1 + \lambda_2 = f_r + ff_h \quad (3-38)$$

$$\lambda_1 \lambda_2 = ff_r f_h - f_r f_k \quad (3-39)$$

$$\lambda_3 = 0 \quad (3-40)$$

The matrices T and T^{-1} are

$$T = \begin{bmatrix} 1 & 1 & 1 \\ \frac{f_r}{\lambda_1 - ff_h} & \frac{f_r}{\lambda_2 - ff_h} & \frac{-f_r}{ff_h} \\ \frac{f_r}{\lambda_1 - ff_h} & \frac{f_r}{\lambda_2 - ff_h} & \frac{-f_r}{f_k} \end{bmatrix} \quad (3-41)$$

$$T^{-1} = \begin{bmatrix} C_1 & \frac{C_1 f_k}{\lambda_1} & \frac{C_1 ff_h f_k}{\lambda_1 (\lambda_1 - ff_h)} \\ C_2 & \frac{C_2 f_k}{\lambda_2} & \frac{C_2 ff_h f_k}{\lambda_2 (\lambda_2 - ff_h)} \\ 0 & C_3 & -C_3 \end{bmatrix} \quad (3-42)$$

$T^{-1}T = 1$ gives

$$C_1 = \frac{\lambda_1 - ff_h}{\lambda_1 - \lambda_2}, \quad C_2 = -\frac{\lambda_2 - ff_h}{\lambda_1 - \lambda_2}, \quad C_3 = -\frac{ff_h f_k}{f_r (f_k - ff_h)} \quad \dots (3-43)$$

Initial and final states of the system are given by

$$U = (f_r, 0, 0) \quad \text{and} \quad U^\dagger = \begin{bmatrix} 1 \\ 1 \\ 1 \end{bmatrix} \quad (3-44)$$

because we consider that the initial segment can be only in the random state and the final segment can be in either of the three states.

Partition function of the system is given by

$$\begin{aligned}
 Z &= U W^{N-1} U^\dagger \\
 &= U T T^{-1} W^{N-1} T T^{-1} U^\dagger \\
 &= C_1 \lambda_1^N + C_2 \lambda_2^N
 \end{aligned} \tag{3-45}$$

Let the fraction of r segments be denoted by $\langle n_r \rangle$, then

$$\begin{aligned}
 \langle n_r \rangle &= \frac{1}{N} \frac{\partial \ln Z}{\partial \ln f_r} = \frac{f_r}{NZ} \frac{\partial Z}{\partial f_r} \\
 &= \frac{f_r}{NZ} \left[NC_1 \lambda_1^{N-1} \frac{\partial \lambda_1}{\partial f_r} + NC_2 \lambda_2^{N-1} \frac{\partial \lambda_2}{\partial f_r} + \lambda_1^N \frac{\partial C_1}{\partial f_r} + \lambda_2^N \frac{\partial C_2}{\partial f_r} \right] \\
 &= \frac{f_r}{Z} \left[C_1 \lambda_1^{N-1} \frac{\partial \lambda_1}{\partial f_r} + C_2 \lambda_2^{N-1} \frac{\partial \lambda_2}{\partial f_r} \right] + \frac{f_r}{NZ} \left[\lambda_1^N \frac{\partial C_1}{\partial f_r} + \lambda_2^N \frac{\partial C_2}{\partial f_r} \right]
 \end{aligned} \tag{3-46}$$

Substituting the values of $\frac{\partial \lambda_1}{\partial f_r}$ and $\frac{\partial \lambda_2}{\partial f_r}$,

$$\begin{aligned}
 \langle n_r \rangle &= \frac{1}{(\lambda_1 - \lambda_2)} \left[\frac{\lambda_1 - f f_h - \frac{C_2}{C_1} \left(\frac{\lambda_2}{\lambda_1} \right)^N (\lambda_2 - f f_h)}{1 + \frac{C_2}{C_1} \left(\frac{\lambda_2}{\lambda_1} \right)^N} \right] \\
 &\quad + \frac{f_r}{NZ} \left[\lambda_1^N \frac{\partial C_1}{\partial f_r} + \lambda_2^N \frac{\partial C_2}{\partial f_r} \right]
 \end{aligned} \tag{3-47}$$

For N large, the above expression reduces to

$$\langle n_r \rangle = \frac{\lambda_1 - f f_h}{(\lambda_1 - \lambda_2)} \tag{3-48}$$

Degree of order or crystallinity is given by

$$Q = 1 - \langle n_r \rangle = \frac{-\lambda_2 + f f_h}{\lambda_1 - \lambda_2} \quad (3-49)$$

Substituting

$$\frac{f_h}{f_r} = S, \quad \frac{\lambda_2}{f_r} = Y2, \quad \frac{\lambda_1}{f_r} = Y1$$

and $\frac{f_k}{f_r} = \sigma$

equation (3-49) becomes

$$Q = \frac{fS - Y2}{Y1 - Y2} \quad (3-50)$$

where $Y1 = \frac{1}{2} \left[1 + fS + \sqrt{(1-fS)^2 + 4\sigma S} \right]$

$$Y2 = \frac{1}{2} \left[1 + fS - \sqrt{(1-fS)^2 + 4\sigma S} \right]$$

$$S = \exp \left[\frac{-\Delta H(T_f - T)}{RTT_f} \right]$$

and $f = \exp\left(\frac{\Delta E}{RT}\right)$

Also $fS = e^{(\Delta H + \Delta E)/RT} e^{-\Delta H/RT_f}$

$$= e^{\Delta H'/RT} e^{-\Delta H/RT_f} \quad (3-51)$$

where $\Delta H' = \Delta H + \Delta E$

Degree of order as a function of temperature at different values of pressure is calculated from the expression (3-50). The heat of transition per mole for a residue from the ordered to the disordered state (trans to gauche)

at one atmospheric pressure is 943.0 Cal./mole. The transition temperature is 410°K. The entropy change associated with the transition is 2.30 Cal./mole/°K and it is assumed to be the same at all pressures. This is justified from the experimental data on entropy of fusion as a function of pressure reported by Matsuoka¹⁵. The deviations from the average value of 2.30 are of the order of 0.10. The heat of fusion, $\Delta H'$ in generating transition curves at different pressure are given in Table 5. These values are taken from experimental results reported in reference 15.

TABLE 5

Pressure (in atmospheres)	Heat of fusion $\Delta H'$ (Cal./mole)	Melting point (°K)
1	943	410
130	952	414
1000	1005	437
2000	1053	458
3000	1101	479

The calculated values of degree of order vs. temperature are given in Table 6 and represented in Figure 10. The general characteristics of melting under the atmospheric pressure are also observed at elevated

TABLE 6

DEGREE OF ORDER VS. TEMPERATURE AT VARIOUS PRESSURES

Temperature °K	Degree of Order Q				
	$\Delta H^{\ddagger}=943$ (Cal./mole) P=1 Atm.	$\Delta H^{\ddagger}=952$ (Cal./mole) P=130 Atm.	$\Delta H^{\ddagger}=1005$ (Cal./mole) P=1000 Atm.	$\Delta H^{\ddagger}=1053$ (Cal./mole) P=2000 Atm.	$\Delta H^{\ddagger}=1101$ (Cal./mole) P=3000 Atm.
375	0.999	0.999	-	-	-
400	0.994	0.996	-	-	-
405	0.977	0.992	-	-	-
410	0.500	0.963	-	-	-
415	0.024	0.218	-	-	-
420	0.006	0.016	-	-	-
425	0.003	0.012	0.995	0.999	-
430	0.002	0.002	0.987	0.999	-
435	-	-	0.884	0.998	-
440	-	-	0.059	0.997	-
445	-	-	0.010	0.996	-
450	-	-	0.004	0.989	0.999
455	-	-	0.002	0.931	0.998
460	-	-	-	0.104	0.998
465	-	-	-	0.013	0.996
470	-	-	-	0.005	0.990
475	-	-	-	0.002	0.954
480	-	-	-	-	0.196
485	-	-	-	-	0.018
490	-	-	-	-	0.006
495	-	-	-	-	0.002

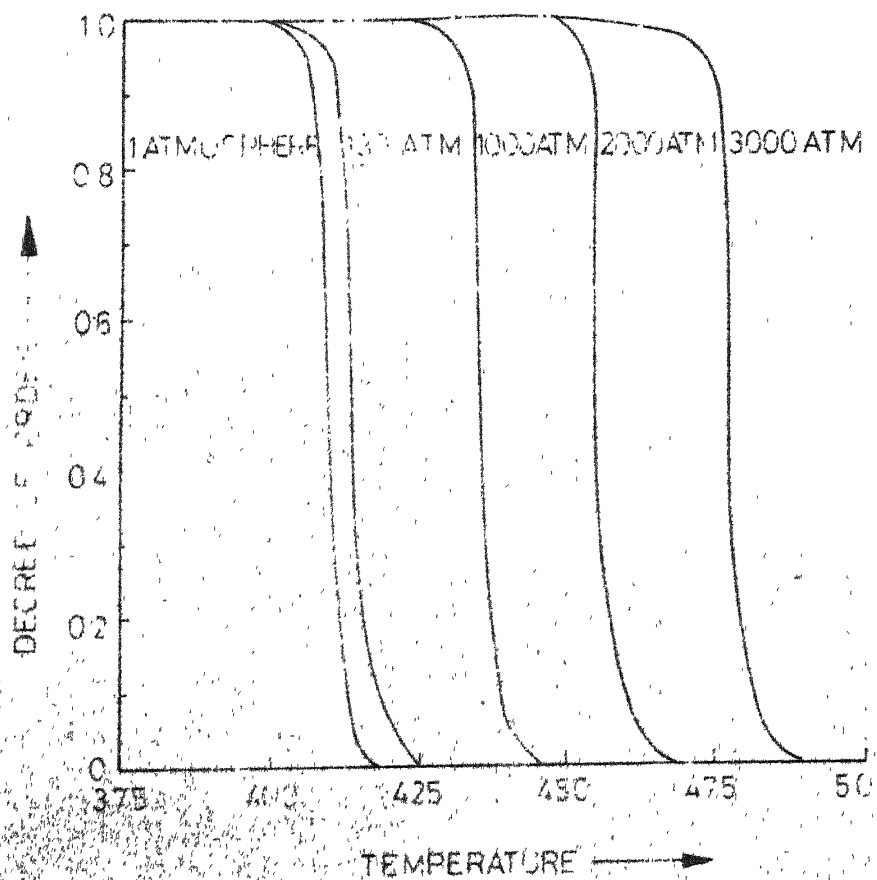


FIG.10 DEGREE OF ORDER VS TEMPERATURE FOR POLYETHYLENE

temperatures. The shift in melting point with pressure is given in Table 5. It is observed that the shift in the melting point with increasing pressure is exactly the same as reported experimentally¹⁵. The general features of the transition curve resemble a step function. It is difficult to make a quantitative comparison with the specific volume versus temperature measurements of Matsuota at different pressures because the dependence of specific volumes for the ordered and disordered state on pressure cannot be easily taken care of. This is partly because the amorphous state itself cannot be uniquely defined and it is evident from the fact that Matsuoka's measurements of the specific volume of the melt varied considerably from sample to sample. Further, it is nowhere specified by the author whether his measurements were carried on a well annealed sample or not. A detailed comparison with his transition curves, therefore, becomes difficult because the history of the sample is not known. An initial distribution of the crystallite size would tend to broaden the transition. Branching has a very large effect on the sharpness of the transition. Due to this the transition becomes very diffuse.

3.5 HELIX-COIL TRANSITION IN A TRICOPOLYMERIC SYSTEM

The cell model for diffuse phase transitions described previously can be modified to explain helix-coil transitions in two and three-copolymeric systems also such as (glutamic acid-lysine)_n and (glutamic acid-lysine-alanine)_n. The modification consists in introducing two or three random and helical states respectively. Considering it specifically for a three-copolymeric system, let the three helical and random coil states be designated by h_1, h_2, h_3 and r_1, r_2, r_3 and the corresponding segment pair partition functions by $f_{h_1}, f_{h_2}, f_{h_3}$ and $f_{r_1}, f_{r_2}, f_{r_3}$ respectively. The k state which represents essentially the boundary tension between helical and random coil states remains the same. Any difference arising due to the different helical states is taken care of by the nucleation parameters $\frac{f_{r_1}}{f_k}, \frac{f_{r_2}}{f_k}$ and $\frac{f_{r_3}}{f_k}$. The Ising matrix for the partition function can be written as

Therefore,

$$\lambda_{\max} = \frac{1}{2} \left[(f_r + f_h) + \sqrt{(f_r - f_h)^2 + 4f_k f_r} \right] \quad (3-56)$$

The expression θ for the fraction of segments in helical states is

$$\theta = 1 - \frac{1 - e^X + 2(f_k/f_r) + A}{A(1 + e^X + A)} \quad (3-57)$$

where

$$A = \left[(e^X - 1)^2 + 4f_k/f_r \right]^{\frac{1}{2}}$$

$$X = (\Delta H_f - T \Delta S_f) / RT,$$

ΔH_f and ΔS_f being respectively the standard heat of entropy of transition per mole of segments from helical to random coil states,

R is the gas constant,

T is the absolute temperature;

$$\text{at the transition temperature } T_m = \frac{\Delta H_f}{\Delta S_f} \quad (3-58)$$

In a recent publication Morita, Simon and Blout¹⁷ have studied transition in (glutamyl-lysyl-alanyl)_n tri-copolymer by measuring optical rotatory dispersion. It was observed that at PH3, the copolypeptides containing 20 mole % or more alanine exhibit a helix content equal to the sum of their alanyl and glutamyl residue contents whereas at

PH8 the helix content equals the alanyl content when the latter is 40 mole % or higher. At lower alanyl contents the electrostatic interaction between charged glutamyl and lysyl residues makes some contribution to helicity. There is helix stabilisation as a result of electrostatic interaction. In addition, hydrophobic interaction also contributes to helical stability. At higher PH value of 12 the amount of helix content observed is proportional to the mole ratio of alanine residues present in the polymer. In fact, at all stages the total helical content is the sum of contributions from alanyl, glutamyl and lysyl residues. The alanyl residues are helix promoters at all PH values whereas the contribution of the other residues depends on their state of ionisation and separation. Morita, Simon and Blout¹⁷ have studied a tri-copolymer with 1:1:3 mole ratio of glutamyl-lysyl-alanyl residues in 8M urea and 5.5 LiBr solution (poly glu²⁰ lys²⁰ ala⁶⁰). When the solution is heated over a temperature range from 5° to 80°C, it undergoes a diffuse transition. At PH = 3, the melting temperature is about 52°C and 39°C at PH = 8. This gives an overall enthalpy change ΔH of approximately -6.4 K Cal./mole in both the cases. This enthalpy change can be calculated from the slope of θ versus $1/T$. The near equality of ΔH for the transition curves at PH3 and PH8 shows that they have identical slopes. The standard enthalpy change, ΔH_f , associated with the

transfer of a single residue from random to ordered state is calculated from the knowledge of nucleation parameter (f_k/f_r). This, in turn, depends on the system and the solvent. In our calculations

$$\Delta H_f = \Delta H \left(\frac{f_k}{f_r} \right)^{\frac{1}{2}} \quad (3-59)$$

$$\text{with } \frac{f_k}{f_r} = 3 \times 10^{-3} .$$

$$\text{and } \Delta H = -6.4 \text{ K Cal./mole}$$

S_f is calculated from equation (3-58) by using

$$T_m = 52^\circ\text{C at PH} = 3$$

$$\text{and } T_m = 39^\circ\text{C at PH} = 8.$$

Using these thermodynamic parameters and expression (3-58) helicity is evaluated as a function of temperature. The results obtained are shown in Figure 11. They are in good agreement with the experimental results of Morita, Simon and Blout¹⁷. The circles and triangles represent the experimental data of these workers for PH3 and PH8 values respectively. The experimental results and theoretical calculations are given in Table 7. The calculated curve shows slight deviations from the experimental points below 295°K. This could be because of the use of approximate and extrapolated data in using the same value of ΔH for both PH values.

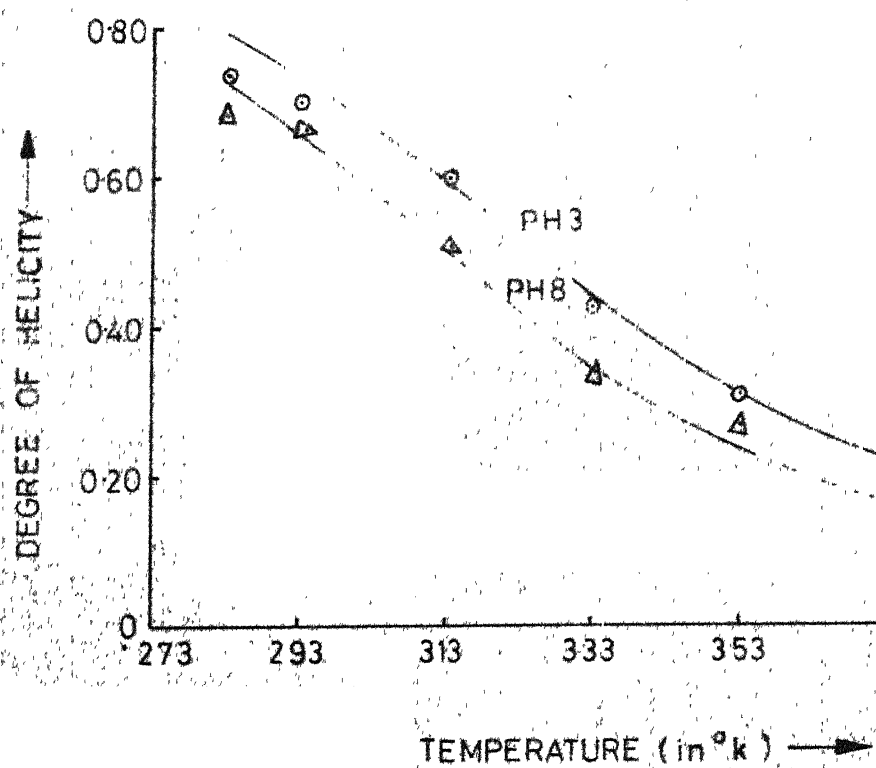


FIG.11. DEGREE OF HELICITY VERSUS TEMPERATURE CURVES
FOR PH3 AND PH8 VALUES.

TABLE 7

Temperature °K	Degree of Helicity θ			
	Theoretical		Experimental	
	PH3	PH8	PH3	PH8
283	0.78	0.72	0.73	0.69
293	0.73	0.65	0.70	0.65
303	0.66	0.57	0.65	0.55
313	0.59	0.49	0.60	0.59
323	0.52	0.41	0.52	0.40
333	0.44	0.35	0.43	0.35
343	0.37	0.28	0.36	0.29
353	0.31	0.24	0.31	0.27

REFERENCES

1. B.H. Zimm and J.K. Bragg, J. Chem. Phys. 31, 526 (1959).
2. S. Lifson and A. Roig, J. Chem. Phys. 34, 1963 (1961).
3. J.H. Gibbs and E.A. Di Marzio, J. Chem. Phys. 28, 1247 (1958).
4. S.A. Rice, A. Wada and E.J. Geiduschek, Discussions Faraday Soc. 25, 130 (1958).
5. T.L. Hill, J. Chem. Phys. 30, 383 (1959).
6. L. Peller, J. Phys. Chem. 63, 1194 (1959).
7. M.E. Baur and L.H. Nosanow, J. Chem. Phys. 37, 153 (1962).
8. L. Landau and E. Lifshitz, Statistical Physics (Oxford University Press, New York, 1938), p. 232.
9. D.C. Poland and H.A. Scheraga, J. Chem. Phys. 43, 2071 (1965).
10. V.D. Gupta and A.K. Gupta, J. Phys. Soc. Japan 20, 841 (1965).
11. A.V. Tobolsky and V.D. Gupta, Ind. J. Phys. 37, 625 (1963).
12. W.F. Seyer, R.F. Peterson and J.L. Keays, J. Am. Chem. Soc. 66, 179 (1944).
13. P.J. Flory, R.A. Orwoll and A. Vrij, J. Am. Chem. Soc. 86, 3507 (1964).
14. P.J. Flory and A. Vrij, J. Am. Chem. Soc. 85, 3548 (1963).
15. S. Matsuoka, J. Poly. Sc. 57, 569 (1962).
16. W.R. Krigbaum, J.V. Dawkins, G.H. Via and Y.I. Balta, J. Poly. Sc. A-2, 4, 475 (1966).
17. K. Morita, E.R. Simon and E.R. Blout, Biopolymers 6, 181 (1968).

CHAPTER - IV

CONCLUSION

In the preceding chapters two main problems on configurational statistics and phase transition have been discussed in two different types of polymeric systems. Both theoretical approaches are subject to several approximations and hence the results obtained have a somewhat limited validity. Taking the first problem regarding the calculation of $\langle R_n^2 \rangle$, expected square of end-to-end distance, the limitations arise from

- (i) the model considered
- (ii) exclusion of excluded volume effects
- (iii) ignoring of chain foldings.

Two models, based on random walk on cubic and diamond lattices have been considered. Of the two models, diamond lattice model is a better approximation because the bond angle ($109^\circ 28'$) is more close to the corresponding angle in polyethylene and hydrocarbons than the bond angle (90°) in a cubic lattice. This makes the description of crystalline and amorphous regions by random walks with and without a preferred scheme all the more approximate on a cubic lattice. The situation is further complicated because the amorphous state itself cannot be uniquely defined. The use of other lattices which are

likely to simulate the polymer structure better would complicate the problem mathematically.

The second approximation is an important one. The interaction between various segments has been completely omitted. In particular, the fact that the same volume element cannot be occupied simultaneously by two units of a polymer chain is not taken into account. In other words, we have not accounted for the forces of repulsion which act between the different segments of the chain that have accidentally approached each other to a very close distance. Montroll¹, and Hijmans and Helleman² have, however, studied the problem in case of a square and a diamond lattice respectively. In the former, first order overlaps resulting from four bonds and in latter enclosures of the pentane type rings have been excluded. Better results have been obtained by a numerical solution using Monte-Carlo method and computer simulation of polymer chain configuration^{3,4}, Edwards⁵ and others have also obtained analytic expressions for the excluded volume problem. The concept of the formation and existence of Lamellar crystallites in bulk crystallized homopolymers, appears to be well founded and supported by electron diffraction and electron microscope observations⁶. On this basis, it is asserted that within an individual crystallite the polymer chains

are folded regularly. The structure of a semi-crystalline polymer is regarded the same as that of a single crystal with the amorphous part representing defects in the crystal. The models presented for the polymer structure in this work do not take care of these modern ideas. However, the theory can be modified to take into account these ideas of chain folding. In such a case when the crystalline regions are regular helices, there can be bond vectors involved in the helix before an advance of one unit in the crystal direction. The chain folding for a square lattice model has been considered by Gupta and Gupta⁷. Lastly, to make an effective comparison with experimental data, a knowledge of the distribution of end-to-end distance and its average value is needed. Besides there are complicating factors like branching.

Coming to the problem of phase transition, the results obtained for the tricopolymer of glut²⁰-lys²⁰-ala⁶⁰ are in much better shape as compared with those for n-paraffin hydrocarbons and for polyethylene. In both cases it is assumed that there exist only two states- helical (crystalline) and random coil (amorphous) whereas in between these two there can be a variety of states. In case of polypeptides one of these states corresponds to the presence of a hydrogen bond (in α - helix) between two given segments of the polymer and the

other to the absence of such a bond between the same two segments. In order to choose an interaction between these two states which corresponds to the physical picture of the process of helix formation, it is clearly necessary to introduce very large repulsions. This is because the existence of one hydrogen bonded state makes it very easy for the next segment to bind itself. In other words, the presence of a bonded state strongly 'repels' the existence of a non-bonded state. This is the physical significance of the nucleation parameter. The possibility of hydrogen-bond formation is due to the relative stiffness of the chain backbone with respect to bending modes. This gives a natural curvature to the polymer so that once a segment is bonded, the probability that the following segment will also be in a position to form a bond is greatly enhanced. Thus, in case of a polypeptide chain, it is easy to understand the physical significance of cooperativity factors as well as the boundary tension term or the nucleation parameter. The structural characteristics in n-paraffin hydrocarbons and polyethylene do not make the physical meaning of cooperativity factor and boundary parameter easy to understand. Cooperativity can be regarded as a result of both intermolecular and intramolecular interactions and the latter should be related to the height of potential barrier in going from one conformation of

bond to another. In case of a finite system the end effects also become important. In such polymeric systems the distinction between ordered and disordered states gets further diffused. There undoubtedly exists a substantial proportion of domains that cannot distinctly be classified as either crystalline or amorphous. The nature of the noncrystalline regions is further complicated by the presence of voids as a direct result of the volume decrease during the late stage of crystallization⁸. Unlike the free volume related to density fluctuations in liquids and amorphous polymers, these voids, or the regions of zero density, cannot be treated as a thermodynamic quantity.

In the case of branched polyethylene, it is further difficult to decide how many carbons in the neighbourhood of either branch points or methyl groups can actually be counted as not participating in the crystalline lattice structure. In studying the effect of pressure on melting curve of polyethylene, there is yet another factor. The overall specific volume below the melting point is not a unique function of pressure and temperature and cannot,, therefore, be treated as a true thermodynamic quantity. In the present calculations, it is the variation of the degree of crystallinity as a function of temperature at various pressures which is used. The results should be compared with the measurements on a linear polyethylene

sample which has been well annealed. The history of the sample thus becomes an unimportant fact. In branched polymers, the width of transition is broadened.

These are thus the unavoidable limitations in the theoretical approach presented in the preceding chapters in studying the configurational statistics and transition in polymeric chains. What is needed is a theory which can take care of not two but many more 'particle states' lying between highly crystalline and completely amorphous states.

REFERENCES

1. E.W. Montroll, J. Chem. Phys. 18, 734 (1950).
2. J. Hijmans and T. Holleman, J. Chem. Phys. 36, 47 (1962).
3. F.T. Wall and J.J. Erbenbeck, J. Chem. Phys. 30, 634 (1959a), 30, 637 (1959b).
4. F.T. Wall and J. Majur, Ann. Acad. Sci. 89, 608 (1961).
5. S.F. Edwards, Proc. Phys. Soc. 85, 613 (1964).
6. A. Keller, Phil. Mag. 2, 1171 (1957).
7. V.D. Gupta and A.K. Gupta, J. Phys. Soc., Japan 20, 423 (1965).
8. P.H. Geil, Polymer Single Crystals, Interscience Publishers (New York) (1963).